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THE MIOCENE FLORA OF IDAHO

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A late Miocene flora which comes from various localities in Idaho furnishes additional evidence, not only of the late age of some of the Columbia lava flows, but also of a well-distributed rainfall at that time, and the presence in that state of many genera of plants which are entirely absent in the recent flora of the region.

This flora was collected by Dr. Virgil R. D. Kirkham from over thirty localities in Nez Perce, Idaho, Kootenai, Lewis, Washington and Latah counties. It is planned to describe its components in detail in one of the United States Geological Survey's "Contributions to Geology."

The collections studied are by no means exhaustive and doubtless many interesting forms still await discovery. Nevertheless, 75 different species of vascular plants have been determined, as well as diatoms, insect leaf galls, fish scales and the valves of fresh-water bivalves. The vascular plants are well distributed among the natural orders, of which 17 are represented, and this fact is another reason for thinking that many more species remain to be discovered. A total of 40 genera have been recognized and these include representatives of 28 families.

The largest genera are Acer, Quercus, Populus, Betula and Laurus, and the maples and oaks greatly outnumber all others in variety. Eighteen of the Miocene genera are no longer present in the northwestern United States. These are Cassia, Castanea, Cebatha, Euonymus, Fagus, Ficus, Glyptostrobus, Gordonia, Liquidambar, Magnolia, Malva (?), Nyssa, Ostrya, Paliurus, Sophora, Taqodium, Tilia and Ulmus.

These genera became Holarctic in their distribution during the Tertiary, and these, as well as many of their associates, have become greatly restricted in their distribution since Miocene times, largely by reason of topographic and climatic changes. In general, they survive in two enormous natural Tertiary forest preserves—the mesophytic hardwood region of southeastern North America, and south central China. Some of these

genera such as the fig, chestnut, beech, sweet-gum, linden and elm have not been restricted to these two regions alone, and others like the bald cypress and Glyptostrobus, have managed to survive in only one of these two regions—the bald cypress in southeastern North America, and its relative, the Glyptostrobus, in China.

Some of these genera are naturally much more interesting than others. Thus Paliurus traces its geological history back as far as the Upper Cretaceous. During the Tertiary it had over a score of species and was present upon all of the continents except Australia and South America. The leaves alone are not conclusively characteristic, but the peltate fruits are highly so, and both are not uncommon from Idaho westward through Washington for a distance of about 200 miles and are quite likely to turn up in the Miocene of adjacent states when these shall have been thoroughly explored. The Idaho species is closest to the existing *Paliurus orientalis* Franchet of Szechwan and Shensi provinces, China. There is a second existing species in Japan, and a third, often called Christ's-thorns, ranges from Spain through southern Europe, Asia Minor and Persia to China.

Another interesting genus is Gordonia. At the present time it has two species in our Coastal Plain between southern Virginia and Louisiana—the loblolly bay—and about 14 additional species in the Asiatic region. Not much of its geological history is known since the leaves of most of the members of the family to which it belongs—the Theaceae or Ternstroemiaceae—are much alike, and fossils of this type are usually referred to a form genus known as Ternstroemites. However, in the Miocene of Idaho and Washington fruits occur with the leaves and the former are very characteristic. So we know that there were Miocene Gordonias halfway between Florida and China, and in Gordonia as in the case of Paliurus these fruits are more like the surviving Asiatic species than they are like those in other regions.

Other associates of Paliurus and Gordonia in the Miocene of Idaho have a somewhat similar history. Both the magnolia and the sweet-gum (Liquidambar) are common throughout our West as late as the Miocene but are today confined to southeastern Asia and southeastern North America, and both go back to the Eocene or earlier. The sour-gum (Nyssa) belongs to a genus with but six or seven existing species in Asia and southeastern North America, but it has about three score extinct species ranging backward in time to the Upper Cretaceous, and Holarctic in their distribution.

Others of these trees of Miocene Idaho are not limited in their modern range to these two regions of China and southeastern North America, but still remain in other regions. Thus the sycamore (Platanus), which was widespread in our western states during the Miocene, has several species in the existing flora but one of which has survived on the Pacific

slope, where, however, it is confined to canyon bottoms and river flood plains in California. The genus has a geological history extending back to the Eocene, and is abundant at the present time in southeastern North America, southwestern Asia and Central America.

Similarly the chestnut (Castanea), formerly abundant throughout the West, has but five existing species—three in southeastern North America, a fourth in China and Japan, and a fifth and Mediterranean species which ranges from Spain to southwestern Asia. A large-leafed species of linden (Tilia) occurs in the Miocene of Idaho and Washington, and its peculiar bracted fruits have been found in an ash bed between lava flows in the Columbia River gorge. Tilia traces its ancestry back to the Eocene. Its score of existing species, variously known as lindens, limes or basswood, are found throughout the North Temperate zone, except in central Asia and western North America, both, generally speaking, regions of geologically late epeirogenic changes and induced arid climatic conditions.

Still other genera found in the Miocene of Idaho have suffered a great diminution in their range since Miocene times, and although they still survive on the Pacific slope, survive in only relict situations. The most frequently cited instance is that of Sequoia which is so abundant in Miocene floras almost everywhere throughout the Northern Hemisphere, and which survives as the redwood and big tree—the first in the rainy coastal strip of Oregon and northern California, and the second in the fog belt on the western slopes of the Sierra Nevada. A second type, common in the Miocene of Idaho and adjacent states is the incense cedar (Libocedrus), which is an old genus represented in existing floras by a few isolated forms in California, eastern Asia, Chile, New Zealand and New Caledonia. The western descendant of the Miocene species, the only one found in North America, is now confined to the Sierran-Cascade coniferous forest region from southern Oregon to Lower California.

The genus Umbellularia, belonging to the same family as our familiar sassafras—the Lauraceae—is abundantly represented in the Miocene of Idaho and adjacent states by several extinct species, and survives as an under and border shrub in the wet redwood forest region of the Pacific coast. The red-bud (Cercis) presents a slightly different situation. The Miocene species of Idaho and Washington has large leaves and very large inflated pods. Its generic history goes back to the lower Eocene, and about two dozen fossil species are known and are found on all of the northern continents. The existing species are but eight in number—Eurasian and North American—and our Miocene species is more similar to the Chinese *Cercis chinensis* than it is to the surviving *Cercis occidentalis*, which is a shrubby chaparral form of dry soils and is confined to California.

The Miocene Hop-hornbeam or ironwood (Ostrya) still survives in the West, but only very locally in canyons in Colorado and Arizona. The

elm (Ulmus), abundant in Miocene Idaho, is found almost everywhere in the North Temperate zone at the present time, except in North America between the Rocky Mountains and the Pacific coast. It was, however, widespread and abundant through the latter region until the progressive aridity brought about by the great elevation of the various mountain chains in post-Miocene time localized and differentiated the once rather generally uniform climate.

These few instances, among many which might be described, show that as late as the upper Miocene the forests of Idaho and adjacent states were essentially a part of a more or less uniform Holarctic forest assemblage, not uniform in details, but containing along with the oaks, maples, birches, etc., sassafras, tulip-trees, walnuts, hickories, ginkgos, sequoias and bald cypress, along with many others, and that the relative impoverishment in genera which the existing flora of this region shows, was due to a lessened and changed rainfall, brought about by differential elevation and changed temperatures. These changes called into existence the so-called Sonoran life zone and the other life zones now recognized in the region, brought about the extinction of many species, and segregated those which managed to survive into regional assemblages such as the Redwood association (heavy rainfall), Chaparral association, stream border association, Desert associations of various types, and all of the other groupings recognized in the region by modern ecologists.

These changes in the floristics were due to post-Tertiary climatic changes, largely induced by post-Tertiary uplift of mountain regions. While this much can be affirmed, the details of the history and the untangling of all of the factors and their method of operation are not so simple, and largely remain to be worked out. At the present time in this part of Idaho as in adjacent parts of eastern Washington, the bulk of the annual precipitation occurs as snow in the winter season, and there is a deficiency during the growing season. Moreover, the latter is shortened and apt to vary greatly from year to year, with droughts in summer and killing frosts at unexpected times.

This fossil flora of Idaho, on the other hand, indicates an ample and well-distributed rainfall, a longer growing season and a generally milder temperature, thus permitting the growth of a typical mesophytic forest cover such as could not survive in the region under present-day conditions.

INTERATOMIC DISTANCES IN COVALENT MOLECULES AND RESONANCE BETWEEN TWO OR MORE LEWIS ELECTRONIC STRUCTURES

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In a paper to be published in the *Zeitschrift für Kristallographie*, Professor M. L. Huggins and I have formulated tables of radii for use in crystals containing electron-pair bonds. With the aid of these tables, we have also constructed a table of radii (table 1) for non-metallic atoms in covalent molecules. These radii are designed especially for purely covalent compounds, in which fluorine forms one electron-pair bond, oxygen two, nitrogen three, etc., but they are applicable also to other compounds, such as $(CH_3)_3N:\ddot{O}:$, with the following exception. The radii given for As, Se, Br, Sb, Te and I are to be used for these atoms with a covalence of one, two or three; for a covalence of four slightly smaller values ("tetrahedral radii") are to be used. The change is probably due to a change in the nature of the bond eigenfunctions involved.

TABLE 1

NORMAL ELECTRON-PAIR-BOND RADII OF ATOMS

SINGLE-BOND RADII

	H			
	0.29 Å (0.375 Å in H_2)			
B	C	N	O	F
0.89	0.77	0.70	0.66	0.64
	Si	P	S	Cl
	1.17	1.10	1.04	0.99
	Ge	As	Se	Br
	1.22	1.21	1.17	1.14
	Sn	Sb	Te	I
	1.40	1.41	1.37	1.33

DOUBLE-BOND RADII

B	C	N	O
0.80	0.69	0.63	0.59
			S
			0.94

TRIPLE-BOND RADII

C	N	O
0.61	0.55	0.52

The values given for C, Si, Ge and Sn are half the observed interatomic distances in the diamond-type crystals, and those for the halogens are half the observed distances in the molecules X_2. The value for hydrogen came from the hydrogen halides. The remaining single-bond radii were obtained by interpolating with the aid of crystal data. The triple-bond radii were obtained by multiplying the single-bond radii by the factor 0.79, which gives agreement with the accurately known C:::N distance in HCN. The factor for double-bond radii was taken as 0.90.

TABLE 2

MOLECULE	RADIUS SUM	OBSERVED DISTANCE	MOLECULE	RADIUS SUM	OBSERVED DISTANCE
ICl	I:Cl = 2.32 Å	2.31 Å			
HCl	H:Cl = 1.28	1.28	O_2 $^1\Sigma$	O::O = 1.18 Å	1.22 Å
HBr	H:Br = 1.43	1.42	H_2CO	C::O = 1.28	1.25
HI	H:I = 1.62	1.62			
			N_2	N:::N = 1.10	1.10
H_2O	O:H = 0.95	0.94*	HCN	C:::N = 1.16	1.16†
NH_3	N:H = 0.99	0.98*	CN	C:::N = 1.16	1.17
CH_4	C:H = 1.06	1.08**	C_2H_2	C:::C = 1.22	1.21‡‡
CH_3F	C:F = 1.41	1.43*			

* From R. Mecke; "Leipziger Vorträge 1931."

** R. G. Dickinson, R. T. Dillon and F. Rasetti, *Phys. Rev.*, **34**, 582 (1929).

† R. M. Badger and J. L. Binder, *Ibid.*, **37**, 800 (1931).

‡‡ From I = 23.509 × 10^{-40} g./cm.^{2} (R. Mecke, *Z. Elektrochem.*, **36**, 803 (1930)) assuming C:H = 1.06 Å.

The comparison of radius sums and observed interatomic distances from band-spectral data given in table 2 shows agreement in general to within about 0.02 Å.

Often two or more reasonable Lewis formulas for a molecule can be written and until recently it has not been possible to reach a confident decision regarding the correct electronic structure in such a case. The comparison of observed interatomic distances with radius sums from table 1 provides considerable information on this point. For example, the two structures :C::O: and :C:::O: for the normal state of carbon monoxide correspond to the interatomic distances 1.28 Å and 1.13 Å, respectively, so that the observed distance 1.15 Å eliminates the first and supports the second. I have recently shown[1] by the study of energy curves, however, that the normal state of the molecule resonates between these two structures, with the triple-bonded structure somewhat more important than the other. Because of the additional energy provided by this resonance, we expect the bond to be stronger than the average for the two structures, and the equilibrium interatomic distance to be smaller than the mean of 1.28 and 1.13 Å. The observed value indicates that *resonance between two or more structures leads to interatomic distances nearly as small as the smallest of those for the individual structures.*

Further support of this is provided by nitrous oxide. The linear configuration NNO with the oxygen atom at one end is supported by the kernel repulsion rule[2] and much chemical evidence, and evidence convincing to physicists has recently been obtained in a band-spectral investigation,[3] which also provided the value I = 59.4 × 10^{-40} g./cm.^{2} for the moment of inertia. Now the usually written electronic structure :N::N::O:, with distances N—N = 1.26 and N—O = 1.22 Å, leads to I = 75.8 × 10^{-40},

and so cannot be correct. A consideration of the energy relations involved indicates :N:::N:O: and :N:N:::O: to be about as stable as the double-bonded structure. These give I = 75.3 and 75.2 $\times 10^{-40}$, respectively. Combining the first and second structures and assuming the N—N and N—O distances to be 1.10 and 1.22 Å, the still unsatisfactory value 66.7 Å is obtained. But the distances N:::N = 1.10 Å and N:::O = 1.07 Å lead to I = 58.1 $\times 10^{-40}$ g./cm.^{2}, in excellent agreement with observation. This corresponds to resonance among the three structures listed above (provided the structure :N::N::O: is included at all), with each interatomic distance equal to the smallest of the values predicted by the various structures. *Both the N—N and the N—O bond behave like triple bonds.*

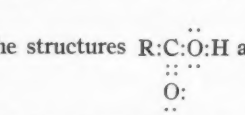
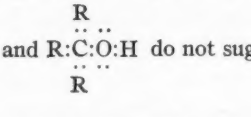
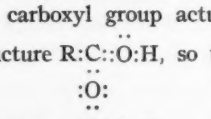
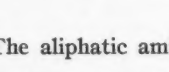
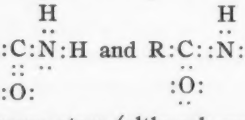
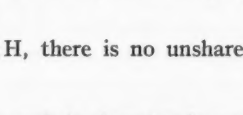
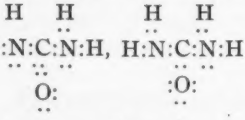
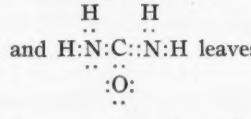
A rough value I = 70 $\times 10^{-40}$ for carbon dioxide from Raman spectra[4] leads to a carbon-oxygen distance of about 1.15 Å. The structure :O::C::O: gives C::O = 1.28 Å, and so is not correct. But if the molecule resonates between this structure and the two other reasonable ones :O:C:::O: and :O:::C:O: the carbon atom would be about 1.13 Å from each oxygen atom.

The observed average distances 1.15 ± 0.05 Å for N_3^- and NCO^- in crystals show that these ions, isosteric with CO_2 and N_2O, also resonate among these three electronic structures.

The value of the carbon-carbon distance in graphite (1.42 Å) and in benzene (1.42 ± 0.03 Å in $C_6(CH_3)_6$) indicates strongly that the bonds are not single bonds (1.54 Å) but are resonating between single and double bonds (1.38 Å), as in the Kekulé structure. No indication is provided as to whether or not other electronic structures contribute significantly to the benzene structure. In the graphite-like crystal BN each B is surrounded by three N's at 1.45 Å, and in the molecule $B_3N_3H_6$, with an atomic configuration like that of benzene, the B—N distance[5] is 1.47 ± 0.07 Å. These values eliminate structures involving single B—N bonds only (1.59 Å), and support resonance between single and double bonds (1.43 Å), as in the carbon compounds.

In many other molecules and ions resonance among several equivalent structures occurs. In CO_3^- and NO_3^- there are three structures of the type :O:C::O: differing only in the choice of the double-bonded oxygen. The observed C—O and N—O distances of 1.25 ± 0.04 Å (C:O = 1.43, C::O = 1.28, N:O = 1.36, N::O = 1.22 Å) indicate the importance of the double bond and of resonance energy in reducing interatomic dis-

tances. The amount of contribution of ionic structures to the normal states of these ions is unknown.

The existence of resonance among several electronic structures leads to direct explanations of many chemical properties of molecules, such as, for example, the acid properties of the carboxyl group as compared with the hydroxyl group. The structures  and  do not suggest that any difference in the oxygen-hydrogen bond should exist. But the carboxyl group actually resonates between this structure and the structure  , so that the hydrogen atom is attached to an oxygen atom which forms a double bond with carbon half the time, in consequence of which ionization takes place easily. Resonance involving double bonds also affects the tendency of a molecule to take up hydrogen ions. The aliphatic amines,  , tend to add a proton to the unshared electron pair of the nitrogen atom. They are accordingly strong bases, forming salts with mineral acids, and they also form complexes with gold, platinum and mercury, the unshared pair forming the bond with the metal atom. In the amides, on the other hand, resonating between the structures  and  , there is no unshared electron pair on the nitrogen atom (although one pair is shared only part of the time), and in consequence these substances are not basic, but have faintly acid properties. Hydrazine, N_2H_4 and the diamines, such as ethylene diamine, $C_2H_4(NH_2)_2$, are di-acid bases, since each NH_2 group can take up one proton. But urea, $CO(NH_2)_2$, is only a mono-acid base, and the proton is added to oxygen rather than nitrogen, for resonance among the structures  ,  and leaves unshared pairs on the oxygen atom alone, and, moreover, gives the oxygen atom greater proton affinity than ketonic oxygen. The amidines, $RC.NH.NH_2$, and guanidines, $C.NH.(NH_2)_2$, are mono-acid bases, the

resonance-migration of the double bond permitting only NH to add a proton.

[1] Linus Pauling, *J. Am. Chem. Soc.*, **54**, 988 (1932).
[2] Linus Pauling and S. B. Hendricks, *Ibid.*, **48**, 641 (1926).
[3] E. K. Plyler and E. F. Barker, *Phys. Rev.*, **38**, 1827 (1931).
[4] W. V. Houston and C. M. Lewis, *Ibid.*, **37**, 227 (1931).
[5] A. Stock and R. Wierl, *Z. anal. Chem.*, **203**, 228 (1931).

THE PENETRATION OF 1-NAPHTHOL-2-SULPHONATE INDOPHENOL, O-CHLORO PHENOL INDOPHENOL AND O-CRESOL INDOPHENOL INTO SPECIES OF VALONIA FROM THE SOUTH SEAS

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The purpose of this investigation was to see whether the oxidation-reduction indicators penetrate other species of *Valonia* in the same way as they do those already investigated.

The species used in these studies were found in the South Seas, namely, *V. ventricosa*, *V. forbesii* and *V. fastigiata*.[1] The dyes used were 1-naphthol-2-sulphonate indophenol, *o*-chloro phenol indophenol and *o*-cresol indophenol. These were dissolved in sea water in a concentration of 0.000097 M. The sea water was buffered with phosphate or borate buffers producing pH values of from 6.3 to 8.1, according to the H electrode. The plants were allowed to remain in these solutions for various lengths of time up to 12 hours or more at a temperature of from 25° to 27°C. At intervals plants were taken out and the sap expressed. The dye was always found in the sap in a reduced form (colorless). The color was brought back by adding a trace of NaOH. The concentration of dye in the sap was measured by comparison with solutions of dye of known concentrations in like-sized tubes. No evidence of injury was noted, such as changes in microscopic or macroscopic appearance or subsequent survival.

It was found that 1-naphthol-2-sulphonate indophenol did not penetrate at any pH value of the external solution used. The remaining two dyes penetrated into the sap in a colorless form. The rate of penetration was dependent in these experiments upon the pH value of the external solution. Penetration was faster from the more acid solutions, decreasing as the sea water became more alkaline. When either of these two dyes came to

equilibrium in the sap, i.e., when the concentration of dye in the sap became constant over a period of several hours, then the concentration of dye in the sap was $^1/_4$ of that in the external solution when phosphate buffers were used, and $^1/_8$ with borate buffers.

These results agree with those found for the species of *Valonia* from Florida, *V. ventricosa*. The laws governing the penetration of these dyes into different species of *Valonia* are essentially alike.

This is a preliminary paper. Details will be published subsequently.[2] Grateful acknowledgment is hereby made to the Bache Fund of the NATIONAL ACADEMY OF SCIENCES for a grant enabling the writer to carry on these experiments in the South Seas.

[1] Kindly identified by Dr. W. A. Setchell.

[2] Brooks, M. M. *Protoplasma*. In process of publication.

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*STUDIES ON MOUSE LEUKEMIA. VI. THE PREDOMINATING CELL TYPE IN LINE I**

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Lymphatic leukemia occurring spontaneously and regularly in mice of Strain C58[10] has been transmitted by inoculation to young mice of the same strain. This has led to the establishment of a series of transmission lines (designated by letters of the alphabet) each with its individual characteristics.[11] Line I has been carried experimentally through 167 transfers in mice of Strain C58 and has shown considerable constancy both in the gross and microscopic pictures and in the interval between inoculation and death. Susceptibility to Line I has been confined to certain strains of mice. A genetic analysis of the susceptibility of Strain C58 to this line has been reported elsewhere.[5,6]

All efforts thus far to separate an active agent causing this leukemia from the cellular component of the inoculated material have been unsuccessful.[9] But the question still remains, whether the cells of the characteristic accumulations in the inoculated animals are descendants of the living cells introduced by inoculation or of cells originating in the host. The following report is a first step in the cytological approach to this problem.

Materials and Methods.—Animals of Strain C58 were taken at 24-hour

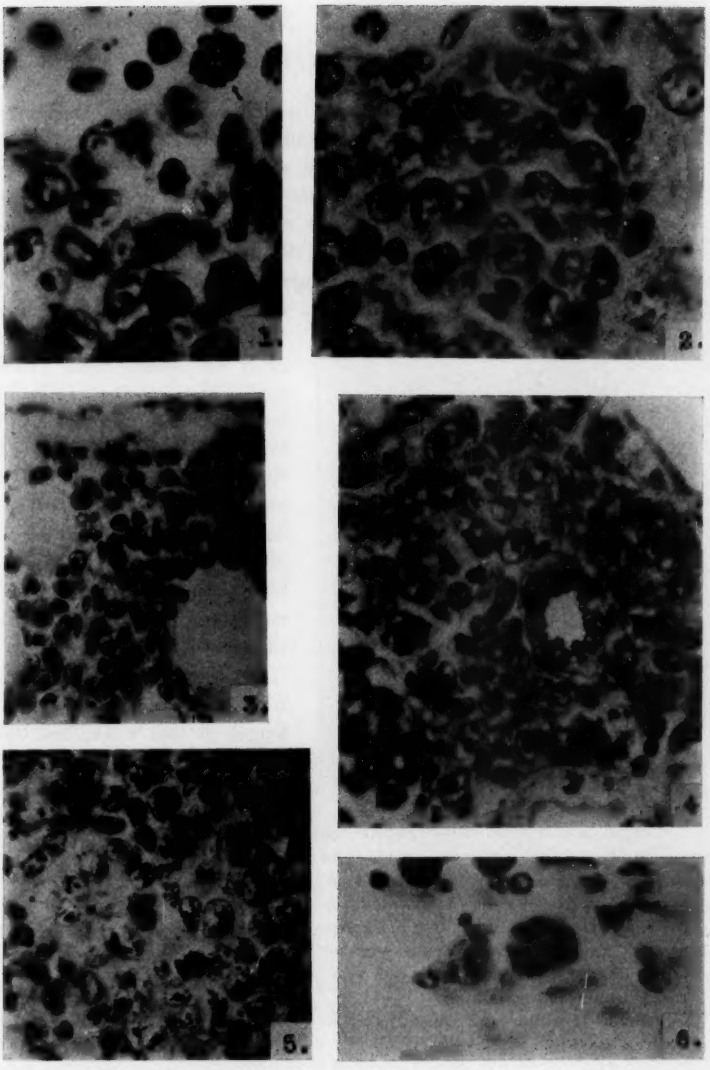


PLATE 1 (Photomicrographs).

Fig. 1. Cells in periphery of follicle in a spleen 96 hours after inoculation. (Polar view mitotic figure in upper right.)

Fig. 2. Portion of perivascular accumulation in liver 72 hours after inoculation.

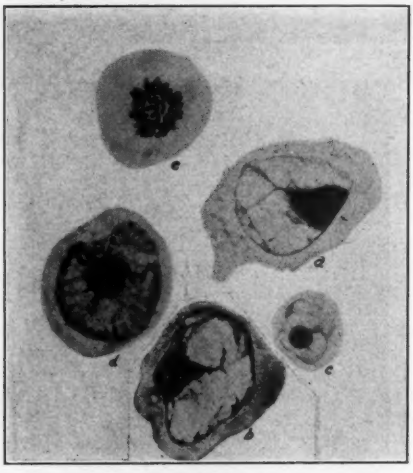
Fig. 3. Infiltration of abdominal wall 96 hours after inoculation.

Fig. 4. Perivascular accumulation in kidney 120 hours after inoculation.

Fig. 5. Dividing cells in a germinal center of a cervical node from an uninoculated mouse of Storrs-Little strain, in which spontaneous leukemia is not known to occur. Cell type indicated by arrows morphologically similar to the active cells of Line I.

Fig. 6. Mitosis in peripheral blood of mouse inoculated with Line I leukemia. Smear preparation, Flemming's fixation and Wright's stain.

intervals after intraperitoneal inoculation with a normal saline suspension of minced spleen from previous inoculations, i.e., the 121st, 122nd, 123rd and 133rd transfers of Line I. In the last of these transfers animals were also killed every four hours during the first twenty-four hour period after inoculation. Tissues were taken at the same time from uninoculated animals as controls to show the activity of the lymphatic tissues of animals in the same environment, of the same age and younger. Tissues from embryos were also examined.



TEXTFIGURE 1

a. Nuclear organization of infiltrating cell from sinusoid of a liver. Drawing made from Feulgen preparation with normal color intensities inverted to emphasize plasmasome. *b.* Cell from perivascular accumulation in kidney. Flemming's triple stain. *c.* Small lymphocyte. *d.* Prophase in infiltrating cell type. *e.* Late prophase chromosomes.

(Camera lucida outlines *a–d* approx. × 2300, *e* approx. × 1900.)

Animals were killed by severing the spinal cord. From each mouse the following material was preserved: lymph nodes, spleen, liver, kidneys, lungs, genitals, abdominal wall and any other tissue that suggested infiltration in the gross picture at autopsy. All tissues were in the fixing fluid within twelve minutes after the death of the animal.

Several methods of fixation were tried in the preliminary stages of this work, but only two were used for routine purposes. Flemming's fluid for twenty-four hours at 3–6°C., and Winge's[13] combination of picro-Carnoy followed by B-15 gave the best results. For special studies the Feulgen reaction was used, as well as fixation and staining according to Schridde.[3,7]

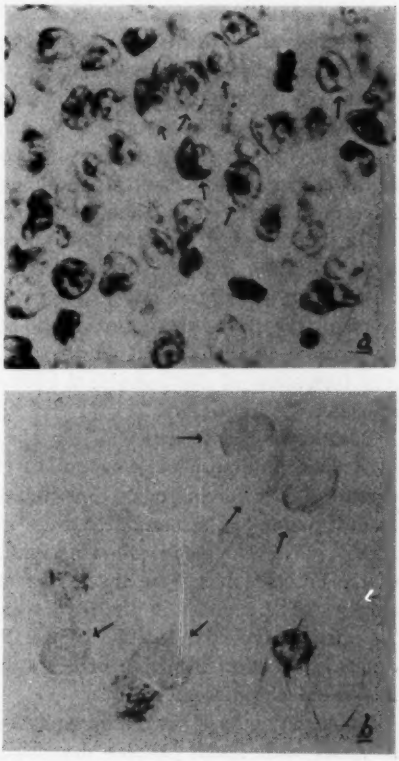
Tissues were embedded in paraffin and cut in serial sections 5 to 7 micra in thickness. All tissues fixed by routine methods were stained either with Haidenhain's iron-alum haematoxylin or with Flemming's triple stain. Part of the embryo material studied was stained with haematoxylin and eosin. Light green was used as a counter-stain following the Feulgen reaction.

Blood and tissue smears were made for staining with Wright's stain, as well as with the technique used by Wiseman[14] for determining the

relative age of lymphocytes. Smears were also fixed with Flemming's fluid followed by staining with Wright's. Observations were made on cells stained supravitally with Janus green and neutral red. Sato's[12] peroxidase method for blood smears was used.

Observations.—The accumulations of cells in the lymphatic tissues and elsewhere appear to consist predominantly of a large type cell of the lymphatic series. This is true of all stages up to the death of the animal. A series of measurements in sectioned material placed the size range of the cell type between 9 and 11 micra when rounded up.

This cell type has a moderate amount of cytoplasm containing many large, round mitochondria (evidenced by supravital staining with Janus green as well as by the Schridde section methods) which, with one or several vacuoles, are usually located near to the nuclear membrane, and have been observed in a number of cases to clump in a position near to the nucleolus. There may be a few azure granules or none at all. Observations on basophilia as described by Wiseman indicated that the majority of the cells were young.



TEXTFIGURE 2

a. Portion of mesenteric node from an inoculated mouse after preparation by the Feulgen technique. Green counter-stain filtered in photographing resulting in faint nucleolar outlines and emphasizing chromatin arrangement. (Photomic.) *b*. Blood smear from inoculated mouse showing negative (arrows) peroxidase reaction. Cells showing positive reaction are polymorphonuclears. (Photomic.)

The nucleus is usually irregular in shape. The position and size of the nucleolus and the arrangement of the chromatin may best be demonstrated by the Feulgen technique, in which the nucleolus

takes a brilliant green from the light green counter-stain in contrast to the purple of the chromatin. The nucleolus is a large, elongated plasmasome, irregular in shape and adherent through most of its length to the nuclear membrane (Textfig. 1*a*). During the "resting" condition the chromatin is dispersed in an open network with a tendency to clump about the nucleolus (Textfigs. 1*b* and 2*a*). The size and position of the plasmasome and the arrangement of the chromatin complement become identifying features of the cell type.

Cell division is found in every section of the areas affected. In some of the earlier stages of infiltration about fifty per cent of the cells involved have been observed in some active stage of division.

During the early prophase the spireme is coarse and is in the form of loops radiating from a point adjacent to the plasmasome. The strands of the loops usually adhere to the nuclear membrane, making it possible to count the strands in optical section (Textfig. 1*d*) and giving a striking appearance to this stage. At the time of fragmentation of the spireme and formation of the individual chromosomes the plasmasome has disappeared entirely.

Because of the tendency of the chromosomes to split precociously at metaphase, late prophase was found to be the best time at which to make counts of the chromosomes (Textfig. 1*e*). A series of fifty counts was made in areas of accumulated cells in different tissues and at various stages of development following inoculation. Camera lucida outlines of the chromosomes were made to facilitate counting and to insure accuracy. The number in the figures examined was invariably forty, the $2n$ number reported for the mouse by Masui,[4] Cox,[1] Minouchi[3] and others. No effort has been made so far to study the morphology of the individual chromosomes.

No variation from normal metaphase and anaphase was observed except in areas with much cellular degeneration. The abnormalities were so rare, however, that they are interpreted as being of no consequence in the continuity of a cell type, but rather the result of abnormal physiological conditions in the degenerative areas. Abnormal mitosis is atypical of most stages of this line of leukemia, and is not comparable in incidence with the chromosomal aberrations reported by Ludford[2] in the cells of a transplantable tumor of the mouse, or with variations reported by Winge[13] in tar carcinomata.

Abnormal "inclusion bodies" have not been observed so far. The peroxidase reaction of the cell type is negative (Textfig. 2*b*).

Observations in the developing liver of mouse embryos and in lymphatic tissues in unweaned and maturing mice of different strains revealed cells of a type morphologically identical to the cell type predominating in the areas of infiltration in the inoculated mice. In the infiltrated areas inter-

mediate stages appear between the cell type described here and the normal small lymphocyte of the mouse.

Summary.—A cytological description is given of the cell type predominating in accumulations in organs and tissues and resulting from experimental inoculation of Line I leukemia. The chromosome number is forty, the normal for somatic cells of the mouse. Mitotic aberrations are not present in significant numbers. None of the cytological methods used differentiated between the cell type described and a morphologically similar type found in normal mouse tissues.

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A CRITIQUE OF RECENT QUANTUM THEORIES. II[1]

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The *sine qua non* of a physical theory is its ability to describe experiential facts accurately and uniquely. But the very first uses of the new quantum mechanics hinted of doubts as to the satisfying of this demand. The special methods employed by Pauli and by Dirac in their solutions of the hydrogen atom were hardly general. The arbitrary number of degrees of freedom used to solve the rotator lacked definiteness. Indeed, the later discovery of the dependence of the integrality of quantum numbers on the dimensions of configurational space indelibly stamped the new methods as heuristic. Perhaps, the obscurity of the source of Schrödinger's equation accounts for the meandering of the stream of thought—a sufficient reason. What is strange, however, is the regarding of the obscurity itself as necessary and the meandering itself as final.

What is ironical, moreover, is the substituting of a definite dilemma for the indefiniteness: namely, that observables are at the same time necessary and impossible. Must we accept this present inadequacy as the ultimate expression of our failure to realize the ideal of theoretical physics? Or would it not be better to have an incomplete interpretation than an interpreted incompleteness, to replace a permanent principle of indeterminacy by a temporary indetermination of principle? Therefore, it is suggested that the applications of the present theories be extensive rather than intensive, critical in expression rather than dogmatic for impression. At least, the following notes are made in such a spirit.

Note I. On the General Equation of Motion.—The classical, canonical equations of motion may be expressed in terms of Poisson's brackets thus:

$$\dot{p}_\kappa = [p_\kappa, H]_{P.B.}$$

and

$$\dot{q}_\kappa = [q_\kappa, H]_{P.B.} \tag{1a}$$

where H is the Hamiltonian function of the generalized coördinates $q\kappa$ and their corresponding momenta $p\kappa$. More generally, for any dynamical function of $q\kappa$ and $p\kappa$, as $x(q\kappa\ p\kappa)$, there may be written

$$\dot{x} = [x, H]_{P.B.}. \tag{1b}$$

Dirac[2] would extend these relations by analogy to quantum mechanics with the reminder that H is to be "well-ordered" and the bracket-expression (introduced in Part I)[1a] is to be used. But is this possible? For equation (1b) is derived in classical dynamics on the basis of (1a). It does not necessarily follow that the same will be true in the twilight region of analogues. A preferable method would be to deduce the analogue of (1b) from those of (1a) assumed as fundamental. We proceed to do this for two general types of functions such as may appear in dynamical theory.

(A) $$x \equiv Kq^k + Lp^l + Mq^m p^n$$

Now
$$\begin{aligned}[x, H] \equiv\ & K\{[q, H]q^{k-1} + q[q, H]q^{k-2} + \ldots + q^{k-1}[q, H]\} \\ & +L\{[p, H]p^{l-1} + p[p, H]p^{l-2} + \ldots + p^{l-1}[p, H]\} \\ & +M\{([q, H]q^{m-1} + q[q, H]q^{m-2} + \ldots + q^{m-1}[q, H])p^n \\ & +q^m([p, H]p^{n-1} + p[p, H]p^{n-2} + \ldots + p^{n-1}[p, H])\}\end{aligned}$$

And
$$\begin{aligned}dx/dt = & K\{(\dot{q})q^{k-1} + q(\dot{q})q^{k-2} + \ldots + q^{k-1}(\dot{q})\} \\ & +L\{(\dot{p})p^{l-1} + p(\dot{p})p^{l-2} + \ldots + p^{l-1}(\dot{p})\} \\ & +M\{[(\dot{q})q^{m-1} + q(\dot{q})q^{m-2} + \ldots + q^{m-1}(\dot{q})]p^n \\ & +q^m[(\dot{p})p^{n-1} + p(\dot{p})p^{n-2} + \ldots + p^{n-1}(\dot{p})]\}\end{aligned}$$

Let
$$\dot{q} \Rightarrow [q, H]$$

and
$$\dot{p} \Rightarrow [p, H]. \tag{2a}$$

Therefore $$\dot{x} \Leftrightarrow [x, H] \tag{2b}$$

And so the equivalence (2b) is established in this instance as a result of the hypothesis (2a). It is due solely to the formal correspondence, noted previously,[1b] between the properties of the bracket-expression and those of the derivative.

(B) $$x \equiv x(q, p, t),$$

where t stands for the time. If the time be treated as a generalized coördinate, classical dynamics shows that the parametric value of the energy (with a negative sign) is the corresponding momentum $(-W)$. Hence, t and $-W$ are canonical conjugates in the same sense as q and p, i.e.,

$$[-W, t] = 1. \tag{3}$$

Therefore $[x, -W]$ is equivalent to the partial derivative of x with respect to t. Consider

$$[x, H - W] \equiv [x, H] + [x, -W].$$

We have just seen that $[x, H]$ is equivalent to the derivative of x with respect to t for all variables except t. (The presence of additional variables does not affect the above result.) Therefore, we may write in this case

$$\dot{x} \Leftrightarrow [x, H - W]. \tag{4}$$

This is the relativistic form of the general equation of motion.

Note II. On the Quantum Conditions.—For the advantage of simplicity we shall consider only one degree of freedom. It can be shown that the equations of motion are sufficient for the deduction of the principle of the conservation of energy and, hence, of Bohr's frequency-relation, from the quantum conditions and from the special type of matrix employed. By a converse derivation the necessity is also established. Van Vleck,[3] however, would show the possibility of interchanging the rôles of the conservation of energy and the quantum conditions in this cycle. The main line of his reasoning is as follows: it can be shown that

$$Hq - qH \equiv h/2\pi i \frac{\partial H}{\partial p}, \tag{1}$$

where $H \equiv H(q, p)$ is the energy. So he considers the relation

$$Fq - qF \equiv h/2\pi i \frac{\partial F}{\partial p}. \tag{2}$$

Obviously this holds for F being H or q; hence, for any function of H and q. But such is p. Therefore, one may write

$$pq - qp \equiv h/2\pi i. \tag{3}$$

This conclusion, however, is subject to two tacit assumptions: that p can be expressed explicitly, as well as rationally, in terms of H and q. Both are not always possible. For example, $H \equiv pq + qp$ is not solvable for p. And as for $H \equiv p^n + Q(q)$, we have

$$p \equiv \{H - Q\}^{\frac{1}{n}}$$

i.e., p is an irrational function to be expanded into an infinite series of H and q. Certainly the extension of a proof applicable only to finite series is unjustifiable without a consideration of convergence, a problem yet to be solved for an infinite series of infinite matrices. And what is more, we note that the usual dynamical system is of this type ($n = 2$).

Note III. On the Matrix Form.—One of the philosophical principles of the matrix mechanics has been its conformity to the doctrine of observables; i.e., that the mathematical expression of physical laws should be in terms of measurable quantities. We note that this has been carried out only in the exponential factor of the matrix element, where the Ritz combination-principle is used. The remaining part is absolute and hence, arbitrary; for measurements always involve differences. Moreover, the form is highly specialized in that all the derivatives with respect to the time either exist or are equal to zero. It is impossible to have cyclic coördinates. So we propose a more general form of matrix which eliminates this difficulty and at the same time conforms just as well to the above doctrine—however desirable this may be. Let

$$q \equiv \| \, q(nm)Q(t)\epsilon^{2\pi i\nu(nm)t} \, \|$$

where $Q(t)$ is single-valued and analytic. Then

$$\frac{d^k q}{dt_k} \equiv \| \, q(nm)Q^k(t)\epsilon^{2\pi i\nu(nm)t} \, \| + \| \, k\{2\pi i\nu(nm)\} \; q(nm)Q^{k-1} \; (t)\epsilon^{2\pi i\nu(nm)t} \, \|$$

$$+ \| \, k(k-1)/2! \{\pi i\nu(nm)\}^2 \, q(nm)Q^{k-2}(t)\epsilon^{2\pi i\nu(nm)t} \, \| + \ldots$$
$$+ \| \, \{2\pi i\nu(nm)\}^k \; q(nm)Q(t)\epsilon^{2\pi i\nu(nm)t} \, \|.$$

To illustrate the use of this form, we shall apply it to a particle, with mass M, moving in the direction of a constant force F.

Now $H \equiv 1/2Mp^2 + Fq.$
Therefore $\dot{q} \equiv 1/Mp$
and $\dot{p} \equiv F$
$\ddot{q} \equiv F/M.$

But $\ddot{q} \equiv \| \, q(nm)Q''(t)\epsilon^{2\pi i\nu(nm)t} \, \| + \| \, 2\{2\pi i\nu(nm)\}q(nm)Q'(t)\epsilon^{2\pi i\nu(nm)t} \, \|$
$+ \| \, \{2\pi i\nu(nm)\}^2 q(nm)Q(t)\epsilon^{2\pi i\nu(nm)t} \, \|.$

Since $\ddot{q}$ is a constant, all the non-diagonal terms must vanish. Consider the diagonal terms ($\nu(nm) = 0$ by definition).

$$q(nn)Q''(t) = F/M$$
$$q(nn)Q(t) = F/2M\, t^2 + At + B,$$

where A and B are arbitrary constants. Thus q and p are diagonal matrices, i.e.,

$$q \equiv \| (F/2M\, t^2 + At + B) \|$$

and

$$p = \| (Ft + MA) \|.$$

Finally, H is determined by these to be a diagonal matrix with all its elements the same along the diagonal. This result agrees with that obtained by classical dynamics, as well as by other quantum theories.

Note IV. On the Linear, Harmonic Oscillator with Damping.—Consider a particle, with mass M, moving along an arbitrary axis under the influence of a restoring force, $-\kappa q$ ($q \equiv$ the distance from the position of equilibrium), and a resisting force, $-\lambda q$.

This problem could be solved directly by the use of our general matrix with its elements involving $Q(t)$ as in the preceding note. But we prefer to take a hint from the classical solution, viz., that the frequency is a complex quantity. Let

$$\nu(nm) = \alpha(nm) + \beta i$$

where

$$\alpha(nm) = \frac{T_n - T_m}{h}, \quad T \equiv \| T_n \|$$

and β is a constant.

Also let

$$q \equiv \| q(nm)\epsilon^{2\pi i\nu(nm)t} \|$$

and

$$p \equiv \| p(nm)\epsilon^{2\pi i\nu(nm)t} \|$$

where q and p are Hermitian.

Consider the canonical equations of motion. In this case

$$H \equiv 1/2M\, p^2 + \kappa/2\, q^2$$

and

$$D \equiv \lambda/2\, \dot{q}^2$$

where D is Rayleigh's dissipation-function. Therefore,

$$\dot{p} \equiv -\kappa q - \lambda\dot{q}$$

and

$$\dot{q} \equiv 1/Mp$$

$\therefore$

$$\ddot{q} + \lambda/M\dot{q} + \kappa/Mq \equiv 0$$

or

$$\left\{ -4\pi^2\nu^2(nm) \frac{+ \lambda 2\pi i}{M} \nu(nm) + \kappa/M \right\} q(nm) = 0.$$

Therefore, $q(nm)$ is zero, unless

$$\nu(nm) = \pm a + bi \tag{1}$$

where $$a \equiv \sqrt{-\frac{\lambda^2}{16\pi^2 M} + \frac{\kappa}{4\pi^2 M}}, \quad b \equiv \frac{\lambda}{4\pi M}.$$

Put $$\nu_0 \equiv \sqrt{\frac{\kappa}{4\pi^2 M}}$$

$$\therefore \quad a \doteq \nu_0 - \frac{\lambda^2}{32\pi^2 M_{\nu_0}}.$$

N.B. For periodic motion $\kappa > \frac{\lambda^2}{4}$.

Consider the quantum condition, i.e.,

$$\sum_j \{p(nj)q(jn) - q(nj)p(jn)\} = h/2\pi i,$$

$$\therefore \quad \sum_j \alpha(nj) \,|\, q(nj) \,|^2 = -h/8\pi^2 M. \tag{2}$$

We shall assume that there is no degeneracy. Then, corresponding to any given n, at least one n' must exist such that $q(nn') \neq 0$. Moreover, $\nu(nn') = \pm a + bi$ so that there are at most two values of n'. Designate these by n'_1 and n'_2. Then

$$\left.\begin{aligned} T_n - T_{n'_1} &= ha \\ \text{and} \quad T_n - T_{n'_2} &= -ha \end{aligned}\right\} \tag{3A}$$

$$\left.\begin{aligned} \text{Or} \quad T_n - T_{n'_1} &= -ha \\ \text{and} \quad T_n - T_{n'_2} &= ha \end{aligned}\right\} \tag{3B}$$

Consider the diagonal terms in H, e.g.

$$H(nn) = 2\pi^2 M\epsilon^{-4\pi bt}(a^2 + b^2 + \nu_0^2)\sum_j |q(nj)|^2. \tag{4}$$

According to the above paragraph, equations (2) and (4) become:

$$\alpha(nn'_1)\{|q(nn'_1)|^2 - |q(nn'_2)|^2\} = -h/8\pi^2 M \tag{2A}$$

and $$H(nn) = 2\pi^2 M\epsilon^{-4\pi bt}(a^2 + b^2 + \nu_0^2)\{|q(nn'_1)|^2 + |q(nn'_2)|^2\}. \tag{4A}$$

Suppose n'_2 does not exist. Hence,

$$\alpha(nn'_1)|q(nn'_1)|^2 = -h/8\pi^2 M \tag{2B}$$

and $$H(n_0n_0) = 4\pi^2 M\nu_0^2\epsilon^{-4\pi bt}|q(nn')|^2. \tag{4B}$$

Therefore, only the first equation of (3B) holds; for (4B) states that $\alpha(nn'_1)$ is negative.

$$\therefore \qquad |q(nn_1')|^2 = -h/8\pi^2 Ma \qquad (2C)$$

and $$H(n_0 n_0) = (h\nu_0^2/2a)\epsilon^{-4\pi bt} \qquad (4C)$$

or $$H(n_0 n_0) \doteqdot (h\nu_0/2)(1 + \lambda^2/32\pi^2 M^2 \nu_0^2)\epsilon^{-4\pi bt}.$$

Thus there is, at most, only one n for which no n'' exists. We shall assume its existence, which can be proved as in the case of the linear, harmonic oscillator without damping. Then there is an n_0' such that

$$T_{n'_0} - T_{n_0} = ha.$$

Let $$n_1 \equiv n_0'$$

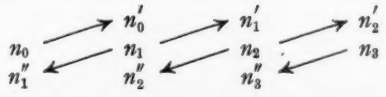
Hence, there are two n's related to n_1 that

$$T_{n'_1} - T_{n_1} = ha$$

and $$T_{n''_1} - T_{n_1} = -ha$$

$$\therefore \qquad n_1'' = n_0.$$

From n_1 can be derived another number n_2, etc., in accordance with the following well-known scheme:



We shall designate any number in this sequence respectively by n_k, where k is any positive integer (including zero). Consider $k \neq 0$. Then equations (2A) and (4A) become:

$$|q(n_k n_{k+1})|^2 - |q(n_k n_{k-1})|^2 = h/8\pi^2 Ma \qquad (2D)$$

and $$H(n_k n_k) = 2\pi^2 M(a^2 + b^2 + \nu_0^2)\{|q(n_k n_{k+1})|^2 + |q(n_k n_{k-1})|^2\}. \qquad (4D)$$

Put $$q_k \equiv |q(n_k n_{k+1})|^2$$

$$\therefore \qquad q_k - q_{k-1} = h/8\pi^2 Ma$$

and $$q_{k-1} - q_{k-2} = h/8\pi^2 Ma$$

finally, $$q_1 - q_0 = h/8\pi^2 Ma.$$

But $$q_0 = h/8\pi^2 Ma$$

$$\therefore \qquad q_k = (h/8\pi^2 Ma)\,(k + 1) \qquad (2E)$$

and $$H(n_k n_k) = (h\nu_0^2/a)(k + {}^1/_2)\epsilon^{-4\pi bt} \qquad (4E)$$

or $$H(n_k n_k) \doteqdot h\nu_0(k + {}^1/_2)\,(1 + \lambda^2/32\pi^2 M^2\nu_0^2)\epsilon^{-4\pi bt}$$

$$\therefore \qquad H(nn) - H(mm) = (h\nu_0^2/a)(n - m)\epsilon^{-4\pi bt} \qquad (5)$$

or $$H(nn) - H(mm) \doteqdot h\nu_0(n - m)(1 + \lambda^2/32\pi^2 M^2\nu_0^2)\epsilon^{-4\pi bt}.$$

We note, however, that the elements of the matrix (save for an arbitrary constant, which we can take to be zero) can be arranged in a series by virtue of relations (3B), so that

$$T_n - T_m = (n - m)ha \tag{6}$$

or

$$T_n - T_m \doteq h\nu_0(n - m)\,(1 - \lambda^2/32\pi^2M^2\nu_0^2)$$

$$T_n - T_m = \{H(nn) - H(mm)\}(a^2/\nu_0^2)\epsilon^{4\pi bt} \tag{7}$$

or

$$T_n - T_m \doteq \{H(nn) - H(mm)\}(1 - \lambda^2/16\pi^2M^2\nu_0)\epsilon^{4\pi bt}.$$

To summarize, we have found states that exist at any instant. If the damping be small ($\lambda \ll 1$), then the values of the energies of these states remain practically constant over a considerable period of time. And equation (7) gives Bohr's frequency-condition to a first approximation. However, the energy of each state is always decreasing. This means figuratively on the basis of Bohr's model that the orbits come relatively closer together as they diminish in size. It is to be noted that the operator-theory of Born and Wiener can be modified similarly to solve this problem. In both cases the quantum condition is a function of the time.

The question arises as to the importance of the problem of damping in atomic physics. Certainly the progress of physics in the past two decades has hardly been cognizant of its value in this domain. Indeed, the truly modern atom is always conservative. And yet, what is a conservative system but one that is either so restricted that it disregards disturbing elements or so unrestricted that it includes them all? The former is too simple for faith; the latter, too complex for reason. The electrodynamic theory of radiation with its damping factor constantly reminds us that even the simple models of classical physics have never been models of such simplicity as is required for the wholly conservative processes of quantum theories. Furthermore, its successes are still too crucial for discard; hence, its methods also. Perhaps, the ultimates of theoretical physics are yet to be taken definitely as uncertain electrons and protons, which may behave as particles or waves, clouds or continua—as the viewer sees fit.

I wish to express my appreciation to Professors Leigh Page and R. Bruce Lindsay for their interest in this project. The latter has also kindly criticized this article. Finally, I am grateful for the Loomis Fellowship of Yale University, which facilitated this work there.

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THE IONIZATION OF ARGON AND NEON BY NEUTRAL ARGON BEAMS

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As a result of the discovery of Kallmann and Rosen[1,2] that the probability of charge transfer is very great for gas ions moving in a gas of their own molecular or atomic species, the possibility of obtaining an atomic beam of high intensity is at once indicated. Since the charge transfer itself takes place without altering the translatory energy of the moving ion, the translatory energy of the formed neutrals will equal that of the ions in case the ion is not scattered, or only slightly scattered. This fact has been utilized to produce beams of neutral argon atoms for the purpose of this investigation.

The apparatus consists of 3 parts. In part I argon ions are formed by electron impact. These argon ions pass through an aperture in a diaphragm of part I and are accelerated between parts I and II by means of a field to give them the desired velocity. By means of an aperture in a diaphragm in part II they pass through the field-free chamber of part II in which argon gas is maintained at a suitable pressure. Between parts I and II the space is evacuated by a high speed pump. In space II the argon ions encounter atoms of argon and neutralize themselves by transfer of charge. From part II the neutral argon beam passes by means of a diaphragm and an aperture into an evacuated space in which a strong retarding field allows only the neutral atoms to pass through a diaphragm into space III. Electrons which might be formed between parts II and III are deflected away by an appropriate transverse field. Thus only neutral atoms of known velocity enter part III.[3] This part constitutes the ionization chamber in which the interaction of the argon beams with argon and neon is investigated at a suitable gas pressure.

In the case of both gases used an exceptionally intense ionization was observed in part III. Both the positive and negative saturation currents were measured. Saturation was obtained in both cases for potentials of ± 4 volts between electrodes in space III lying parallel to the beam and protected by a sort of guard ring from secondary electrons. No measurement of the intensity of the primary atomic beam was undertaken in these preliminary experiments.

The results obtained were as follows.

Neutral Argon Atoms in Argon.—The number of positive and negative carriers produced by the neutral beams was nearly the same (negative carriers being slightly predominant). This fact indicates that in general

only slow argon ions had been formed in part III. Had the atoms of the beams been ionized they would have left the space as positive ions subsequently leaving the region of part III. Thus the positive ion current would have been much smaller than the negative current in part III.

This result and the general result given later on might allow the conjecture that the newly formed neutral atom-beam is not in its normal state, a point which has still to be proved and which might vary the following theoretical considerations.

Neutral Argon Atoms in Neon.—In this case the positive charges collected in part III were relatively feeble in comparison with the negative charges collected. This finds its most natural explanation in the assumption that it is the larger argon atom of lower ionizing potential (which constitutes the beams) that is ionized. They escape from the measuring field of part III leaving only their electrons behind. Thus the currents measured are predominantly due to the electrons generated.

General Result and Conclusions.—A most important common factor underlies the results described in the two cases above. In both cases (argon in argon and argon in neon) it appears that in the region of velocities from 50 to 120 volts equivalent velocity of the neutral argon atoms the intensity of the ionization is practically constant, and decreases but slowly at the lower velocities. This suggests that even at an equivalent velocity of thirty volts the course of the curves will be practically unaltered, the value of about 30 volts being the ionizing potential for argon atoms in argon as it would follow from the law of conservation of momentum.

If one compares the observed sharp inset of ionization of argon-like K^+ ions in argon which occurs at 96 volts with these new results for argon atoms in argon one sees the enormous difference between the ionization potentials which are to be ascribed to the difference in nuclear charge since the electron configurations as well as the masses of K^+ and A are practically the same.

This new phenomenon suggests the following explanation of the ionization experiments. When the potassium ion has approached close enough to the argon atom the two together might be regarded for a short time as a pseudo molecule. The ionization potential of such a pseudo molecular-ion is higher than that of the pseudo molecule itself.[4]

It thus appears possible through a consideration of these experiments to explain the results found in the ionization of the inert gases by slow alkali ions.[5] The high values of the inset of ionization in this case[5] are to be ascribed to the nuclear charge while the maximal effect might be ascribed to the law of conservation of momentum since the transfer of impulse (and thereby the degree of interpenetration) must be greatest for individuals of equal mass. Further fine details of the process must in all

probability be sought in the effect of polarization of the neutral atom and the electron configurations of the atoms involved.

But the independent conclusions we might draw from these experiments reach much further than giving us only the possibility of explaining the results on the ionization of the noble gases by positive alkali ions.[5]

Since the experiments indicate that ionization by neutral beams takes place with large efficiency even at low energies, a new field of investigating thermo-ionization is opened by this method. Results in this line might, later on, gain importance in the question of chemical reactions. The possibility is also suggested of selecting from Maxwell's distribution curve of velocities in gases a certain desired velocity.

Furthermore, these results are of the greatest importance for the phenomena of discharge in gases. The rôle which in the past has been ascribed to the positive ion but which seems inconsistent with the high value recently[6] found for the energy required to enable a positive ion to begin to ionize at all may now easily be transferred to the neutral atoms. For the positive ion may very readily transform itself to a neutral atom which may then easily ionize atoms or molecules even at very low velocities.

These investigations will be published in detail when quantitative data resulting from the measurement of the intensity of the neutral beams has been obtained.

In conclusion, I wish to acknowledge that Prof. Fritz Zwicky, to whom I owe in the course of the last year many interesting and helpful discussions on theoretical questions of the ionization of the inert gases by positive alkali ions, has originally suggested this experiment in order to prove the correctness of his considerations given in the following paper.

* William G. Kerckhoff Fellow.

[1] H. Kallmann and B. Rosen, *Zeits. Physik*, **61**, 61 (1930); **64**, 806 (1930).

[2] H. Kallmann and B. Rosen, *Naturwissenschaften*, **18**, 867 (1930).

[3] The possibility of neutral argon beams obtained by neutralization of double ionized argon, which would have twice the energy is only very low.

[4] See the following paper of Fritz Zwicky.

[5] The maximum yield, the lowest ionization potentials and the steepest rise of the ionization curve has been shown to occur for that ion that lies nearest the inert gas to be ionized in the periodic table. Otto Beeck, *Annalen Physik*, [5] **6**, 1001 (1930); Otto Beeck and J. C. Mouzon, **11**, 737 (1931); **11**, 858 (1931), and other places to be found there.

IONIZATION IN GASES BY IONS AND ATOMS

By F. Zwicky

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Communicated March 1, 1932

It has been assumed for a long time that the ionization of atoms by ions must in one form or another play an important rôle in the phenomena of gas discharges. This assumption found its mathematical expression in the well-known theory of Townsend. Only recently, however, have the elementary effects of the ionization by ions been experimentally investigated. The ionization of noble gas atoms by alkali ions was studied in particular and a number of important results have been arrived at by R. M. Sutton,[1] R. M. Sutton and J. C. Mouzon[2] and O. Beeck.[3]

The points which are essential for our considerations may be stated roughly as follows. Denote the masses of the impinging ion and the target gas atom by m and M, respectively. With the auxiliary condition that the energy of the impinging ion be kept constant

$$mv^2/2 = K = eV \tag{1}$$

we obtain these results:

(1) The efficiency of ionization has a maximum for the ion whose mass comes nearest to satisfying the relation

$$m = M. \tag{2}$$

(2) For $m \gtrless M$ the efficiency γ of ionization falls off both sides. It is significant, moreover, that it falls off much more rapidly for $m < M$ than for $m > M$, i.e., that

$$\gamma_{M+m_1} > \gamma_{M-m_1}. \tag{3}$$

(3) The efficiency of ionization has a general tendency to increase both with the masses of the impinging ion and the atom which is to be ionized.

(4) The potential V_i at which the ionization first sets in is lowest for $m = M$.

We try now to find an interpretation for the observations (1) to (4). It is known that the ionization of atoms by not too slow electrons ($V >$ 100 volts) can be accounted for by calculating the momentum J which is directly transferred from the impinging electron to an electron of the atom which is hit. If ϵ_P is the ionization potential of the target atom, an electron will be ejected from this atom if the momentum transferred to it satisfies the inequality

$$J^2/2\mu > \epsilon_P \tag{4}$$

where μ is the mass of an electron.

Such a procedure is legitimate in this case because a not too slow electron traverses the atom in a time which is considerably shorter than the period of revolution of the bound electrons.

In the case of an ion impinging on the gas atom, however, the duration of the impact is much greater than the period of the bound electron. Indeed, we may picture the interpenetration of the two particles as a perfectly elastic process. The duration τ of the impact then is independent of the relative velocity of the two particles, as τ may in the first approximation be looked upon as the period of an elastic oscillation which is independent of the amplitude. We may put approximately

$$\tau = \pi\left[\frac{mM}{f(m + M)}\right]^{1/2}. \tag{5}$$

The elastic constant f (force for a displacement of 1 cm.) will be of the same order of magnitude as the elastic constant which characterizes the binding of the two atoms in a diatomic molecule, HCl for instance. We thus will have this order of magnitude

$$\tau = 10^{-12} \text{ seconds} \tag{6}$$

whereas the period of revolution of an electron is of the order 10^{-15} sec.

The impinging ion therefore causes an adiabatic disturbance in the gas atom in the form of an elastic wave, which is similar to the elastic waves which are set up in colliding billiard balls. The ionization of the atom then might be compared to the rupture of one of the billiard balls. On this simple picture the efficiency of ionization evidently will depend on the following two conditions:

(α) The elastic wave set up in the atom will transfer a certain maximum effective momentum J_{eff} to one of the atom's bound electrons. If

$$J_{\text{eff}}^2/2\mu > \epsilon_P \tag{7}$$

the electron will be ejected.

(β) The ionization potential ϵ_P in this case will be characteristic for the "freak" molecule formed for an instance by the two colliding particles at the time of closest approach or at the time of reversal of that component of the relative velocity which lies in the connecting line of centers of the two particles.

We now ask how the essential quantities J_{eff} and ϵ_P might be determined.

The elastic wave set up in the atom will be determined by the hardness of the impact (maximum force of repulsion F) and its duration τ. We shall have roughly

$$J_{\text{eff}} \propto \tau F \propto J \tag{8}$$

where J is the transfer of momentum from the impinging ion to the gas atom. It is

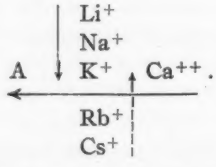
$$J = 2M\sqrt{2K}\, m^{1/2}/(m + M) \qquad (9)$$

if no permanent internal transformations occur in the two particles. If we observe the condition expressed in equation (1) J will be maximum for $m = M$, which fact therefore suggests itself as an explanation for the observations (1) and (4).

The continuous rise of the efficiency of ionization with m and M cannot be explained with momentum considerations alone, as J is not sufficiently asymmetrical with respect to $m = M$. The observations (2) and (3) therefore suggest a decrease of ϵ_P with m and M. This is, of course, to be expected, as the "freak" molecule formed for an instant will be characterized by an ionization potential for its loosest electron which changes essentially in the same way as the ionization potentials of the particles which are colliding. These ionization potentials decrease with increasing mass in the same column of the periodic system.

These simple considerations then seem to account roughly for the principal features of the ionization of noble gas atoms by alkali ions. It also is very important that they allow us at once to draw some very interesting and far-reaching conclusions. Indeed, as the ionization potential of the "freak" molecule formed must change essentially in the same way as the ionization potentials of the colliding particles we conclude that *the ionizing power of a particle increases with decreasing charge if mass and kinetic energy are held the same.* The freak molecule formed will have either the character of a neutral diatomic molecule if two neutral particles collide or of a molecule-ion if an ion hits an atom. We arrive therefore at the remarkable conclusion that *if we let A, K^+, Ca^{++}, etc., of the same kinetic energy impinge on A-atoms the ionizing power must decrease as we go from A to K^+ and Ca^{++}, etc.* The ionization of argon, for instance, by particles of constant kinetic energy therefore increases in the directions indicated by the arrows in the following scheme.

Ionization of argon by



The crucial test for the correctness of our considerations evidently consists in trying whether or not the efficiency of ionization of argon by fast argon particles is greater than the efficiency of ionization by K^+ ions of the same energy.

It was known to me from the experiments of F. M. Penning[4] and others that neutral argon atoms up to speeds corresponding to several hundred volts may be obtained by shooting A^+ ions through argon gas. Some of the A^+ are neutralized by an exchange of electrons taking place with the argon atoms of the bombarded gas. Those particles which are neutralized without being deflected also retain their original energy. As it seemed possible in this manner to produce beams of neutral A atoms with speeds corresponding to several hundred volts I proposed about a year ago[5] to try the experiment of ionizing argon by fast argon particles. Dr. O. Beeck of our Institute, who was well equipped to carry out this investigation, very kindly took up my suggestion and successfully accomplished the difficult experiment. The preliminary results which he has obtained check very well with the predictions which I based on the above considerations. For the details of the experimental arrangement and the results obtained so far I refer the reader to Dr. Beeck's paper in this same issue of the PROCEEDINGS.

It is desirable of course to investigate the ionizing power of doubly charged ions also and to bombard noble gas atoms other than argon in order to establish more firmly the correctness of the theoretical considerations given here. So far these conceptions have well served their purpose as a guiding viewpoint for furthering our knowledge of ionization phenomena. There is no doubt, however, that they will have to be refined and that a more complete theory must be worked out in order to account for all the details of the phenomena in question. Indeed the statement of the experimental results given in the points (1) to (4) represents only a crude approximation to the really observed phenomena which have been described in detail in previous publications by Dr. Beeck.

A few remarks concerning the weak points of the considerations given may not be out of place.

In the first place it seems fairly clear that J_{eff} will not depend merely on the momentum J transferred from the impinging particle to the gas atom. J_{eff} in fact is the product of the time of duration of the impact multiplied by a certain average of the force $\bar{F}$ acting during the impact.

$$J_{\text{eff}} = \tau \bar{F} \tag{10}$$

Now τ is maximum for $m = \infty$ as appears from (5). On the other hand $\bar{F}$ is maximum for $m = 0$ whereas the product J is maximum for $m = M$. It is to be anticipated that J_{eff} will depend not only on J in a wholesale fashion but will also be affected somehow or other by τ and $\bar{F}$ individually. Such effects have here not been considered.

In the second place it is to be expected that the charge will have some effect in the formation of J and J_{eff}. Indeed due to its polarizing power

the atom hit by an ion will not only be distorted by the impact but also by electric polarization. Furthermore, the resulting relative speed will not be exactly given by the initial speed v, but instead there will be an additional velocity due to the attraction which results from the energy of polarization

$$-\alpha e^2/r^4 \qquad (11)$$

where α is the polarizability of the atom which is hit and r the distance between the two particles.

Thirdly, as mentioned before, we have neglected the elastic wave inside of the atom in calculating the momentum transferred.

Finally the effective ionization potential will not depend simply on the ionization potentials of the two particles involved. A more exact theory will have to take into account the more characteristic properties of the outer shells of the colliding particles and their dynamic behavior during the impact.

It seems probable that the above considerations can be generalized to ionization and dissociation processes produced by collisions of ions and atoms with molecules.

The results obtained so far promise to be of the greatest importance for our understanding of many phenomena in gas discharges, thermal ionization, etc., possibilities which have been pointed out by Dr. Beeck in his paper.

I am indebted to Drs. Sutton, Mouzon and Beeck for having called my attention to the problem of ionization by ions and for the first-hand information which I obtained from Dr. Beeck during many mutual discussions.

[1] R. M. Sutton, *Phys. Rev.*, **33**, 364 (1929).

[2] R. M. Sutton and J. C. Mouzon, *Phys. Rev.*, **35**, 695 (1930).

[3] O. Beeck, *Ann. Physik*, **6**, 1001 (1930); O. Beeck and J. C. Mouzon, *Ann. Physik*, **11**, 737 (1931).

[4] F. M. Penning and C. F. Veenemans, *Zeitschr. Physik*, **62**, 746.

[5] The essential points of this paper were presented during a discussion at the American Physical Society meeting at the University of California at Los Angeles, December 12–13, 1930.

THE MASS OF THE ELECTRON

BY WILLIAM DUANE

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Communicated February 24, 1932

The mass of the electron, m_0, may be estimated by means of a single experiment. We use in this estimate two theoretical formulas (*a*) Bragg's formula for the reflection of x-rays by a crystal,

$$\lambda = 2d \sin \Theta$$

and (*b*) Bohr's formula for the Rydberg constant,

$$cR_\infty = \frac{2\pi^2 e^4 m_0}{h^3}.$$

For the last sixteen years or so I have been using for the grating constant of calcite (100 planes) $d = 3.028 \times 10^{-8}$ cm. A few years ago Birge, in his extensive paper on the general physical constants (*Physical Review*, Supplement, July, 1929), came to the conclusion that for calcite, $d = 3.0283 \times 10^{-8}$ at 20°C. and, correcting for various orders of reflection, that, for the first order, the effective grating space, $d = 3.0279 \times 10^{-8}$. Very recently, Bearden (*Physical Review*, December 15, 1931) published a new estimation of this grating constant of calcite and gave the value 3.0278 Å at 18°C. for the reflection of x-rays in the first order. The slight variation for different orders corresponds with the observations published by Patterson and the writer (*Physical Review*, 1920), following Stenstrom. I am inclined to think, therefore, that the value of d which I have been using is the best four-figure value for the first few orders of reflection.

Some years ago we measured the value of h by means of the reflection of x-rays by a calcite crystal (Duane and Blake, *Physical Review*, December, 1917, p. 624; Duane, Palmer and Yeh, *Proceedings of the National Academy of Sciences*, August, 1921, pp. 237–241). In these researches we used the above-mentioned Bragg formula with $d = 3.028 \times 10^{-8}$ cm.

The formula for calculating h is the quantum equation of Einstein, $Ve = hc/\lambda$, which applies to the short wave-length limit of the continuous x-ray spectrum (Duane and Hunt, *Physical Review*, August, 1915, p. 111), and for which the Bragg equation gives λ.

In estimating the value of "h" by means of x-ray reflections we assume a value for the electron charge, "e." Since, however, $e^{1/3}$ enters into the calculation of the grating constant of calcite, what we really determine by means of the x-ray reflection measurements is $e^{4/3}/h$.

In each of the two measurements of h above referred to the experiments consisted only in the measurement of an angle and that of a voltage. The angle was measured in the ordinary way, by means of a divided circle and vernier. The voltage was measured in one experiment by comparing it with the voltage of a standard cell by means of a potentiometer, the manganin resistances of which were very carefully measured and the insulation of the circuits was made similar to the insulation used in delicate electrostatic experiments. This experiment gave $e^{4/3}/h = 5.689 \times 10^{13}$.

The estimate of the percentage error made in measuring something usually amounts to nothing more than a guess, especially when the number of values obtained is very small. I have usually thought that the above value of $e^{4/3}/h$ may contain a probable error of approximately $1/20$ of 1%. In estimating this value of $e^{4/3}/h$ the very small correction suggested by Birge for the fact that the absolute value of the volt instead of the commercial value should be used has been made.

Using the above value of $e^{4/3}/h$ and using also Bohr's expression for the Rydberg constant we can calculate immediately the mass, m_0, of the electron. Bohr's equation for the Rydberg constant is

$$cR_\infty = \frac{2\pi^2 e^4 m_0}{h^3}.$$

The errors in the measurement of the Rydberg constant and of the velocity of light are so small that we may neglect them and we may take for the value of cR_∞

$$cR_\infty = 3.2899 \times 10^{15}.$$

Calculating m_0 from these two expressions and from our experiment on x-ray reflection we get $m_0 = 9.054 \times 10^{-28}$. The mass, m_0, estimated in this way depends only on one set of experiments, the measurements of h, assuming the Rydberg constant and Bragg's expression for λ to be given.

If we take the experimentally determined value of e/m_0 we can calculate the value of e. We may also determine h from the x-ray experiments. In 1930, Charlotte T. Perry and Professor E. L. Chaffee measured the value of e/m_0 without using the electric or the magnetic deflection of electron particles (*Physical Review*, **36**, September 1, 1930, pp. 904–918). These experiments were carried out in our Cruft Laboratory and consisted in the comparison of the velocity of electrons with the velocity of very short Hertzian waves. The electron rays were produced by the constant voltage coming from our very high-tension storage battery. The voltage applied was measured exactly as we had measured voltages in our above-mentioned research on the value of h, comparing it with a standard cell by means of a potentiometer including the same very high

resistances which we had previously used. These resistances were re-checked and found to have changed by a negligible amount during the twelve years. Using the value of the electron energy as given by the voltage, and the velocity measured, the authors determined $e/m_0 = 1.7606 \times 10^7$ abs. e. s. u. Using this value of e/m_0 and the above value of m_0, e turns out to be $e = 1.5940 \times 10^{-20}$ e. m. u. $= 4.779 \times 10^{-10}$ e. s. u. This value of e differs from that given by Millikan by less than his estimate of his experimental errors. We may also re-calculate h from our experiments and find that $h = 6.568 \times 10^{-27}$. These values of e and h lie close to those recently estimated by W. N. Bond (*Philosophical Magazine*, September, 1931).

Since the date on which Professor Chaffee and Miss Perry published their researches several other measurements of e/m_0 have been made. J. S. Campbell and W. V. Houston made a measurement and they presented their results to the Physical Society at a meeting held in Los Angeles, California (*Physical Review*, **37,** January 15, 1931, p. 228). In their researches the ratio e/m_0 is determined from the Zeeman effects in two spectral lines, one of zinc and the other of cadmium. They think the measurements with the zinc line are slightly more accurate than those with the cadmium line. For the zinc line value of this ratio they give $e/m_0 = 1.7577 \times 10^7$ e. m. u. Using this value of e/m_0 and our value of the mass of the electron charge, the charge e, in e. s. u. turns out to be $e = 4.771 \times 10^{-10}$, a value slightly less than the average value given by Millikan. With this value of e we may re-calculate from our experiments the value of h, which turns out to be $h = 6.553 \times 10^{-27}$.

The most recent estimate of the value of e/m_0 made in Germany is described by Fritz Kirchner in the *Annalen der Physik* (5 volge, 1932, Band 12, Heft 4, pp. 503–508). Kirchner gives for the value of e/m_0

$$e/m_0 = 1.7585 \times 10^7.$$

This value lies between those used above in making the two calculations of e and h. Using it in the calculations we get the following values of e and of h:

$$e = 4.773 \times 10^{-10} \text{ e. s. u.}$$
$$h = 6.557 \times 10^{-27}.$$

These values appear to be very nearly correct according to our present knowledge of electrical measurements.

To sum up, the rest mass m_0 of the electron has been calculated from the experiments that we performed a number of years ago in determining the value of h. In this estimate of m_0 ($m_0 = 9.054 \times 10^{-28}$) the following three theoretical formulas have been used: (*a*) Bragg's formula for the reflection of x-rays by calcite, $d = 3.028 \times 10^{-8}$ cm.; (*b*) Bohr's formula

for the Rydberg constant, the value of the Rydberg constant being $cR_\infty = 3.2899 \times 10^{15}$ cm.; and (*c*) Einstein's quantum equation. The experimental values of e and of h are not used in this calculation of m_0, nor are the results of any other experiments than ours on the reflection of x-rays by calcite, and the experimental determinations of the fundamental constants d and cR_∞. From our value of m_0 and from measurements by others of e/m_0 we can calculate first e and then h.

AN INSTRUMENT FOR THE PHOTOMETERING OF THE NEW X-RAY LINES

By William Duane

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Communicated March 4, 1932

In the Proceedings of the National Academy of Sciences for January, 1932, appears an article in which I describe experiments on the new K series x-ray lines, of which I spoke in a paper presented to the American Physical Society at its New York meeting in February, 1931. The end of the article contains several photometer curves of the β doublet, the γ line and a few of the new lines belonging to the molybdenum K series spectrum. The photometer now existing in the Jefferson Laboratory produced some of these curves, and for the other curves it gives me great pleasure to thank Dr. DuMond of the California Institute of Technology.

Recently I have designed and had set up in our new Physical Research Laboratory a photometer for drawing curves of x-ray spectra. The photometer contains some new features. Figure 1 represents the instrument. At the extreme right of the figure appears a box of considerable size, which contains a high powered electric lamp (a one-kilowatt lamp, for instance). The photographic negative of the x-ray line spectrum to be examined by the photometer lies just below "*a*." An accurately ground lens system made by Leits for producing microphotographs lies at "*b*" and projects the spectrum lines to the vertical front side of a small metal box at "*c*." In this particular case the two lines of the β doublet in the K series of molybdenum appear at "*c*." The photograph resembles one of those shown in the previous article (New Lines in the K Series of X-rays, The Proceedings of the National Academy of Sciences, Vol. 18, No. 1, pp. 63–68, January, 1932). The two β lines appear clearly separated from each other although the difference between their wave-lengths amounts to only 0.000563 Å.

I have used the well-known photo-electric cell to examine the lines. The lines are horizontal. Just below them is a horizontal black line in the figure at the center of which lies a very narrow horizontal slit in the side of the small metal box. The metal box contains the photo-electric cell just behind the slit. The positive anode of the photo-electric cell is joined to earth through the metal box, all connections being soldered. The inner negative surface of the cell, from which the electrons proceed, is connected to the negative pole of a battery contained in the larger metal box "*d*." To complete the electrical circuit of the photo-electric cell, the positive pole of the battery is joined through a heavily insulated,

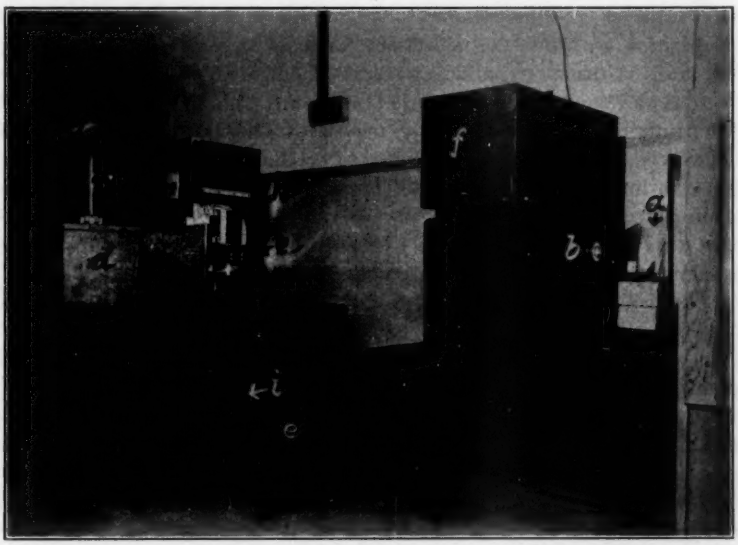

FIGURE 1

lead-covered wire "*e*" to a d'Arsonval galvanometer in the large iron box "*f*." The second terminal of the galvanometer is joined by separate wires to the box "*f*" and then to earth. The lead covering of the circuit "*e*" is soldered to the box "*d*" and to the box "*f*." There is, therefore, a complete circuit running through the photo-electric cell, the battery and the galvanometer, and this entire circuit is completely protected from electrical disturbances by the metal boxes and the lead covering of the wire circuit. The galvanometer deflection is observed by means of a beam of light coming from the lamp "*g*" (which has in front of it a narrow vertical slit). This beam of light after passing through an opening in the far side of box "*f*," is reflected from the galvanometer mirror to a scale at "*h*."

At this scale lies a long narrow horizontal slit held fixed in space. Behind this slit at "*h*" is an undeveloped photographic plate in a light-tight box, fixed in space and having the fixed slit "*h*" in its front surface. The plate lies in a vertical plane. It and the photo-electric cell with its slit lying just behind the projected spectrum lines are mechanically joined together. They lie on a vertical holder which can be moved slowly up and down by means of a worm gear and suitable screw mechanism lying on the floor at "*i*" between the concrete supporting blocks. As the photo-electric cell and its slit move up or down the slit crosses behind the image of the lines at "*c*," and, as the light entering the cell varies, the photo-electric current varies and the galvanometer deflection at "*h*" varies. During this variation the undeveloped photographic plate behind "*h*" changes its position and thus the deflection, corresponding in magnitude to the blackness of the spectrum negative, traces out a curve on it. Evidently there is an exact one to one relation between the points on this curve and the points in the image of the spectrum lines, and no elaborate system of cogwheels, etc., is necessary in order to get the proper relations between the coördinates of the curve—an important characteristic of the new photometer I am describing. The slit at "*c*" has a breadth of only 0.2 mm. and as the β doublet has a breadth of approximately 20 mm. the machine produces curves corresponding to very high resolution.

The photo-electric cell in the metal box is one that has a maximum of sensitivity in the neighborhood of the visible wave-length 5500 Å. It gives me great pleasure to thank Mr. Ives and Mr. Olpin of the Bell Telephone Research Laboratory in New York for this photo-electric cell. They very kindly spent some time in preparing a cell that would have its maximum sensitivity in the section of the spectrum that produces the greatest effect on the human eyes. Since this light belongs to a fairly narrow band, there is very little error due to the lens system, which is highly corrected for the most visible light. This facilitates properly focusing the spectral lines at (*c*) and reduces any error that may be due to lack of focus. This point has been investigated by taking curves with precisely the same negative of the β doublet, one curve with a beam of light the wave-lengths of which did not differ from each other very much, and a second curve with a beam containing a much larger number of different wave-lengths. In the former curves the portion between the β_1 and β_2 lines appears to be much less intense than in the latter.

In making detailed studies of the errors which may be produced in drawing the above-mentioned curves I have had taken a great many photographs. The errors may be classified somewhat as follows:

Figure 2 contains curves representing the two lines in the β doublet belonging to the K series of molybdenum shown in figure 1. I have had the curves of figure 2 produced in such a way as to illustrate the various

errors that may occur in making measurements; which errors must be guarded against and corrected.

The uppermost curve in this figure 2, aa', was photographed with a solid black body in front of the slit c (Fig. 1). During the drawing of this line the photo-electric cell, its slit and the photographic plate were lowered through a distance of about 4 cm. During this motion no light entered the photo-electric cell and aa' appears to be perfectly straight and to contain no jiggles. Early photograph records of this kind did contain jiggles which have been eliminated. The fact that the line is now straight means that there are no mechanical jars, no variations in the current passing through the photo-electric cell and no changes of zero of the d'Arsonval galvanometer capable of producing changes in the galvanometer's deflection of sufficient magnitude to be seen.

The two curves bb' and cc' represent the current through the photo-electric cell when light was allowed to enter and when its slit moved up and down, back of the projections of the β doublet. The curve bb' corresponds to motion downward and the curve cc' to motion upward. I have had these curves drawn purposely in such a way as to illustrate the effects due to the galvanometer's period and damping. The speed of taking one of the curves (four minutes from a to a') was purposely made fairly large and so also was the period of the galvanometer (sixteen seconds).

FIGURE 2

The dots lying between these two curves represent static deflections. To produce one of the dots, the light reflected from the galvanometer's mirror was shut off and the photo-electric cell was raised 1 mm. After sixteen seconds the galvanometer needle had come to rest and the light reflected from its mirror was allowed to pass through the slit h long enough to register on the photographic plate. It was then cut off, and the slit raised another millimeter in order to take another point, etc., etc. A line drawn through these points would represent a static curve. The curves in the figure are shifted, one to the right and one to the left of the static curve, this shift being due to the fact that owing to the period of the galvanometer, its deflection lags slightly behind the motion of the slit and photo-electric cell. The curve is shifted to the right or to the left according to whether it is being produced in the right hand direction or in the left hand. By decreasing the speed at which the curves are drawn or by decreasing

the period of the galvanometer the curves may be caused to approach each other and become superposed as illustrated in figure 3.

Although the two curves bb' and cc' appear superposed at points on the β peaks, they become separated at their right hand ends near c'. This separation occurs in the vertical direction and cannot be due to the period of the galvanometer. The separation comes from a slight decrease in the voltage of the storage battery that was delivering current through the projection lamp. The curve bb' was taken in the direction from b' to b, and then the curve in the opposite direction from c to c' was taken. The velocity was so small that nearly ninety minutes of time elapsed between the instants corresponding to the two right hand ends of the curves. Toward the end of this period the battery ran down slightly and cc' at its end represents a slightly smaller deflection than bb'.

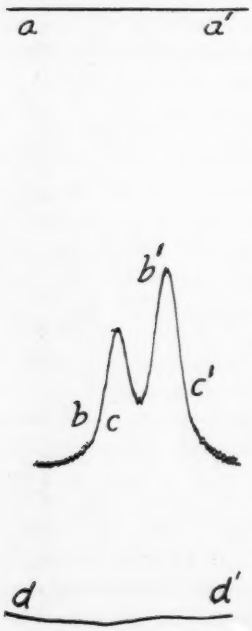

FIGURE 3

For many purposes I feel that it is best not to reduce the horizontal shift between the two curves so as to make them absolutely coincide in order to detect any variations in the curve which may be purely transient. If the curves are very nearly superimposed upon one another variations that appear up or down at corresponding points on both curves must be due to the variation of the light coming through the photographic negatives which are permanent and not transient.

Curve dd' represents the variation of the photo-electric current after the photographic negative had been removed. Its variations correspond to changes from point to point in the intensity of the beam of light striking and passing through the photo-electric slit. As illustrated in figure 3 the intensity of this light has been made much more uniform. A correction for the variation in intensity, however, may be obtained obviously by dividing the distances from aa' to bb' by the corresponding distances from aa' to dd'.

As stated above the reason for designing this photometer, and for having it constructed and set up, has been to examine in some detail the x-ray K series spectrum in which I have found a number of new lines. The new lines were presented to the Physical Society at the New York meeting in February, 1931. They appear also on the photographs reproduced in the previous article in the January number of the PROCEEDINGS of the

National Academy of Sciences. The new features of the x-ray spectrum include (*a*) a band apparently containing a number of lines somewhat shorter than the delta line (*O-K* electrons), which may be due to conductivity electrons in the molybdenum target falling into the K position; (*b*) a line called "*x*" half way between β doublet and the γ line, (*c*) a line very close to the β_1 line and on the short wave-length side of it and (*d*) various very weak lines on the sides of the β lines and of the γ line, especially a long series of satellites on the short wave-length side of the β_1 line. According to the photographs, however, these rows of satellites must extend on both sides of the main K series lines. Apparently they prevent the curves from falling to zero between the β_1 and β_2 lines and between the γ and δ lines.

Professor Patterson of the Troy Polytechnic was at Harvard as a NATIONAL RESEARCH FELLOW some thirteen years ago and was working on the x-ray line spectra. He made some observations which led him to suggest that there might be weak satellites of this kind near the strong lines themselves. We therefore tried to get by the ionization methods which we were using at that time, definite and completely satisfactory evidence for the existence of such satellites. We did not obtain evidence by the ionization method that was completely satisfactory. The photographs of the K series of molybdenum, however, which I presented a year ago to the Physical Society at its New York meeting in February and which were discussed in the article in the January, 1932, PROCEEDINGS and in this article, seem to furnish evidence in favor of their existence.

Obviously the above-described photometer may be employed to examine spectra in a variety of ways. For instance, a large photograph of the spectral lines may be taken by means of an ordinary projection lantern and then this large photographic negative may be placed before the photo-electric cell slit at *c* (Fig. 1). Then, illuminating the part of the negative which one wishes to examine by means of a powerful lamp at some distance from the photometer, the photo-electric slit may be moved up or down and a photographic curve taken of the spectral lines. This method has enabled us to study more thoroughly the faint lines in the molybdenum spectrum referred to above. Some of the curves thus obtained will be published later, together with wave-length measurements of the lines.

Professor P. A. Ross of the University of Stanford has recently published two letters in the *Physical Review* (February 1, and February 15, 1932), in which he mentions some extraordinarily interesting ionization curves representing the K series spectrum of molybdenum. He verifies by these ionization observations the above-mentioned new lines in the K series of molybdenum. He also finds similar lines in the K series of other chemical elements (Tel—Pal—Ag—Cd—Sn— and Sb). Obviously this discovery is of very great importance. The suggestion by Professor Ross

that some of the new lines may correspond to so-called forbidden lines will greatly interest those who like to look in that way at lines that are not explained by the electron theory.

THE PRESSURE VARIATION OF THE HEAT FUNCTION AS A DIRECT MEASURE OF THE VAN DER WAALS FORCES

BY FREDERICK G. KEYES AND SAMUEL C. COLLINS

CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY. SERIAL NO. 291.

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The heat function or thermodynamic potential, $\chi = \epsilon + pv$, where ϵ is the energy, p the pressure and v the volume, is a function of the greatest importance in the applications of thermodynamics to chemistry and engineering. In the present note a brief account will be given of a direct method whereby it has been found possible to determine the change of χ with pressure at constant temperature.

The differential coefficient $\left(\frac{\partial \chi}{\partial p}\right)_T$ possesses among other properties a most intimate relation to the departure of gases from the simple equation $pv = RT$. It will be shown that the coefficient is most closely related to and is, in fact, a measure of, the molecular van der Waals forces, attractive and repulsive, operative in giving to gases their known physical properties.

Starting with Gibbs' equation (90)[1] we find

$$\left(\frac{\partial \chi}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + v + \Sigma \mu_1 \left(\frac{\partial m_1}{\partial p}\right)_T \qquad (1)$$

where S, μ and m represent the entropy, the thermodynamic potential and the mass. The change of entropy with pressure under the conditions of constant temperatures is equivalent to $-\left(\frac{\partial v}{\partial T}\right)_T$ assuming the state of the system to be only a function of the variables P and T. In the special case of a single pure substance (1) becomes,

$$\left(\frac{\partial \chi}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{\partial v\tau}{\partial \tau}\right)_p, \qquad (2)$$

where τ is used to denote T^{-1}.

The Joule-Thomson coefficient, $\left(\frac{dT}{dp}\right) = \eta$, is given on the other hand

by the formula

$$\eta = -\frac{\left(\frac{\partial \chi}{\partial p}\right)_T}{\left(\frac{\partial \chi}{\partial T}\right)_p} = -\frac{\left(\frac{\partial \chi}{\partial p}\right)_T}{C_p}. \qquad (3)$$

It is evident therefore that an experimental method capable of giving precise values of $\left(\frac{\partial \chi}{\partial p}\right)_T$ will lead to values of the heat capacity where Joule-Thomson data are available. It is to be noted also that an empirical knowledge of the p–v–T properties is obtainable, for setting $\left(\frac{\partial \chi}{\partial p}\right)_T$ equal to C we find from integrating (2)

$$\left[(v\tau)_1 - (v\tau)_2 = \int_{\tau_1}^{\tau_2} C d\tau\right]_p. \qquad (4)$$

Thus if the value of $v\tau$ be known, say along the vapor saturation curve, values of v at higher temperatures are deducible for constant pressure from a knowledge of the C's. If the method of obtaining the latter is simple and moderately exact, very exact values of the volumes of the fluid can be deduced. If at the same time η values are available, a very convenient method of obtaining the heat capacity, C_p, over a range of temperature and pressure becomes possible.

For an ideal gas $\left(\frac{\partial \chi}{\partial p}\right)_i$ is zero. However, for an ideal gas mixture having convertible components the coefficient would have a finite value. Thus considering the simple case of the reaction $2A \longleftrightarrow A_2$ where α is used to represent the fraction of the A molecules converted to A_2 we obtain for $\alpha \longrightarrow 0$,

$$\left(\frac{\partial \chi}{\partial p}\right)_i = \frac{R\alpha}{2p}\left[\left(\frac{\partial f(T)}{\partial \tau}\right)_p - T\right] \qquad (5)$$

where $\frac{\partial f(T)}{\partial \tau}$ is proportional to the heat,

$$-(\Delta U^\circ + \Sigma \nu_i \int C v_i dT)$$

required to convert $2A$ to A_2. An experimental value of $\left(\frac{\partial \chi}{\partial p}\right)_p$ would therefore determine α provided the heat of the reaction were known or should α be known values for the heat of the reaction may be derived.

Actual gases having convertible components are, of course, far from ideal but the method here proposed promises, at least in those cases where

the reaction velocity is large, to be a convenient and accurate means of determining the properties of such mixtures. Further and more detailed discussion of this subject will be resumed in a later communication.

The procedure used in the present investigation, $\left[\left(\frac{\partial \chi}{\partial p}\right)_T \text{positive}\right]$, consists in allowing the gas to escape under a measured pressure through a platinum capillary tube into a region of lower pressure while generating heat in the capillary electrically to maintain the system at constant temperature. The electrical energy is expended in the wall of the capillary itself and if the bore and cross sectional area of the wall are uniform the expansion of the gas is isothermal.

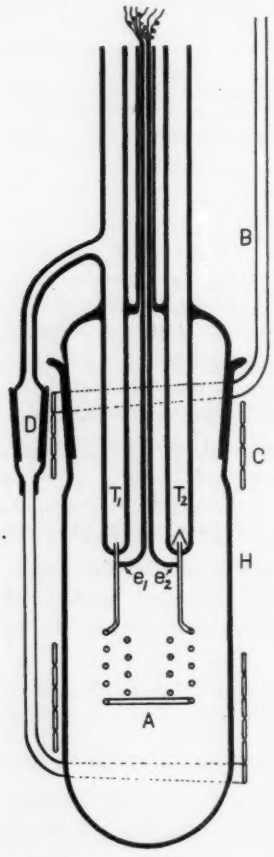

FIG. 1. Calorimeter.

The apparatus is represented in the figure. The calorimeter shell H and thermometer tubes T_1 and T_2 are made of pyrex glass. To facilitate assembly and adjustment of the parts, the shell is made in two pieces which can be united by means of the ground joint. B is a thin-walled copper tube 12 meters in length and 5 mm. in diameter, the greater part of which has been flattened and wound into a coil C. This coil serves to bring the temperature of the incoming gas substantially to that of the bath which surrounds the apparatus. From the copper coil the gas passes through the ground joint D (metal to glass) to the thermometer tube T_1 in which is suspended a platinum ribbon constituting a resistance thermometer. The thermometer is unsheathed so that the winding is in actual contact with the gas stream. T_1 communicates with T_2 through the platinum capillary tube A which is one meter long, 0.5 mm. in bore and 0.1 mm. wall thickness.

Expansion of the gas occurs in the capillary. In case there is a tendency to cool (the method as here described is applicable only to those cases in which there is a fall in temperature), electrical energy is brought in through current leads made of No. 24 copper wire and contained in the cables e_1, e_2. A second thermometer

(similar to that in T_1) in T_2 indicates the temperature of the outgoing gas. The fall of pressure across the capillary is measured by a mercury manometer, the two arms of which are connected to the heads of the thermometer tubes.

From T_2 the gas is led through a suitable absorption train where it is collected for measured intervals of time and weighed. The amount of heat supplied to the capillary is computed from potentiometer measurements of the voltage drops across the capillary and across a standard resistance in the same circuit.

Under ordinary operating conditions the temperature of the capillary has been found to be about one-third degree higher than that of the bath. Because of the temperature gradient a small fraction of the heat escapes to the bath. The space surrounding the capillary is highly exhausted so that heat may only be lost by radiation to the walls and by conduction from the ends of the capillary. The loss of heat is quite small but must be taken into account.

The pure platinum capillary is used as a resistance thermometer, the resistance being computed from the current and potential drop measurements made during the experiment. The current leads e_1, e_2, are double and during the measurements the heating current is borne by the two leads in parallel. For the blank run a current approximately half as large and supplied by a separate battery is caused to flow along one of the current leads and back through its double without entering the capillary. The same is done with the double leads at the other end of the capillary. These currents will produce about the same heating effect in the leads as the original current during the experiment. A third current is now superposed upon the others and directed through the capillary to bring its temperature to the desired magnitude. Its energy value is the correction that has been applied to the experimental results.

Two gases have been used thus far: CO_2 and NH_3. The observed values of $\left(\frac{\partial \chi}{\partial p}\right)_T$ as well as those calculated by means of an equation of state for the gases[2] are tabulated below:

UNITS: ATMOSPHERES, C. CM. PER GRAM, DEGREES K.

	T	p (MEAN)	$\eta c_p = -\left(\frac{\partial \chi}{\partial p}\right)_T$ OBSERVED	CALCULATED
CO_2	300.23	2.459	8.889	9.037
NH_3	300.23	1.890	58.542	58.589
	300.23	1.511	58.212	58.245

The experimental values are in excellent agreement with the values computed by means of the equation of state based on p–v–T data at higher pressures. Unless the observed quantities are affected by unrecognized

errors they appear to be reliable to about 1 in 200 which at the low pressures of the measurements corresponds to very precise p–v–T data. Thus in the case of NH_3 at 1.9 atm. consistent p–v–T data to about 1 in 7000 would be required to enable $\left(\frac{\partial \chi}{\partial p}\right)$ to be computed to within 1 part in 200. The method in fact appears to be especially adapted to low pressure and low temperature experimentation; a particularly desirable feature since the technique of making p–v–T measurements is complicated, time consuming and at low temperatures difficult. The low temperature region is of course quite important from the point of view of extending the existing knowledge of the van der Waals forces.

The relation of the quantity $\left(\frac{\partial \chi}{\partial p}\right)_T$ or $\left(\frac{\partial v\tau}{\partial \tau}\right)_p$ to the intramolecular or van der Waals forces may be exhibited by using the equation of state in the form,

$$p = \frac{RT}{v - B}$$
$$B = 2\pi N \int (1 - e^{-\epsilon/kT}) r^2 dr. \tag{6}$$

The classical expression[3] for B is valid for low pressures but not too low temperatures[4,5] where quantized collision states become of sufficient importance to require consideration.

The expression for $\left(\frac{\partial v\tau}{\partial \tau}\right)$ using (6) becomes $\left(\frac{\partial B\tau}{\partial \tau}\right)$, a function of T alone. If B is computed for the classical van der Waals' molecular model there is obtained:

or
$$\frac{\partial B\tau}{\partial \tau} = \beta - \frac{2A}{RT} - 3a_1 \frac{A^2}{RT}\frac{1}{\beta}$$
$$B = \beta - \frac{A}{RT}\left(1 + a_1 \frac{A}{RT\beta} + a_2 \frac{A}{RT\beta}\right) \tag{7}$$

where β is the four-fold volume of the molecules, A corresponds to the a of van der Waals' special form of equation and a_1, a_2, ... are constants calculable when the law of attractive force is known.

It is clear from the foregoing that the present method of determining $\left(\frac{\partial \chi}{\partial p}\right)_T$ may be regarded as a direct experimental procedure for obtaining exact information regarding molecular forces in gases. It is evidently particularly convenient for investigations at low temperatures; a region where values of the effects of the van der Waals forces and data for gaseous heat capacities[6] is of great importance in guiding theoretical developments.

Equation 6 can be formulated for the case of a mixture of non-convertible

or non-reacting gas mixtures, thus enabling values of $\left(\frac{\partial \chi}{\partial p}\right)_T$ for such mixtures to be used to guide the equation of state theory for mixtures. This is of interest, for a complete knowledge of the van der Waals forces in mixtures is of profound importance in the application of thermodynamics to chemical equilibria at finite pressures.

[1] J. W. Gibbs, *Scientific Papers*, Vol. I, p. 87.

[2] J. A. Beattie, *Proc. Amer. Acad.*, **63**, 229 (1928); *J. Math. and Phys. M.I.T.*, **9**, 11 (1930).

[3] K. F. Herzfeld Muller Pouillet, *Lehrbuch der Physik*, **3**, 161; also F. G. Keyes, *Chem. Rev.*, **6**, 175 (1929).

[4] J. G. Kirkwood and F. G. Keyes, *Phys. Rev.*, **38**, 516 (1931).

[5] J. G. Kirkwood, *Phys. Zeit.*, **33**, 39 (1932).

[6] An innovation in the technique of measuring the Joule-Thomson effect to be reported later has been developed which is adapted to low temperatures and low pressures. From the two effects $\left(\frac{\partial T}{\partial p}\right)_\chi$ and $\left(\frac{\partial \chi}{\partial p}\right)_T$ the value of c_p is immediately deducible. (Eq. 3.)

PROOF OF GIBBS' HYPOTHESIS ON THE TENDENCY TOWARD STATISTICAL EQUILIBRIUM

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In this paper the author applies the circle of ideas due to B. O. Koopman[1] and J. v. Neumann[2] to the proof of Gibbs' fundamental hypothesis concerning the tendency of an ensemble of independent systems toward statistical equilibrium.[3] The motions of the systems are described by a Hamiltonian differential system,

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}.$$

The ensemble is represented by a certain distribution in phase $f(P)dm$, where $P = (p_i, q_i)$, and where $dm = \pi dq_i dp_i$ is the invariant volume element in the phase space. The distribution is carried by the phase flow associated with (H) and will, in general, alter in time. Under what conditions has (H) the property that any initial distribution tend toward a permanent one (not affected by the motions, i.e., being invariant under the flow)? Simple examples show that this tendency does not always exist.[3] After giving an appropriate mathematical formulation of the tendency toward permanent distributions the author derives various necessary and sufficient conditions that a given flow show that tendency.

Let P denote the points of a general space Ω (not necessarily associated with (H)), and let $T_t(P)$,

$$T_sT_t = T_{s+t},$$

be a linear one parameter group of one to one transformations of Ω into itself (steady flow on Ω) preserving a certain measure m on Ω in the sense of Lebesgue. We set

$$(f, g) = \int_\Omega f(P)g(P)dm, \quad \|f\| = \sqrt{(f, f)},$$

for any two q. s. f. (quadratically summable functions) $f(P)$, $g(P)$. Only functions with real values are considered in this paper. All integrals are to be understood in the sense of Lebesgue. According to B. O. Koopman[1] the symbol U_t, where U_tf signifies the function $f(T_t(P))$, defines a linear one parameter group of unitary operators in the Hilbert space of all q. s. f. $f(P)$,

$$U_sU_t = U_{s+t}, \quad (U_tf, U_tg) = (f, g).$$

A function f is called invariant under the group T_t if, for any given t, $U_tf = f$ holds almost everywhere on Ω. We shall use the following theorem proved by v. Neumann:[2]

Time-Average Theorem.—Every q. s. f. $f(P)$ possesses a time-average $f^*(P)$ such that

$$\lim_{T=\infty} \left\| \frac{1}{T} \int_\alpha^{\alpha+T} U_tf dt - f^* \right\| = 0,^4$$

independently of $\alpha = \alpha(T)$. $f^*(P)$ is q. s. and invariant under the group.

The equation

$$(f, h) = (f^*, h) \tag{1}$$

is fulfilled by any q. s. and invariant $h(P)$.[5]

Let $f(P)dm$ be any initial ($t = 0$) distribution on Ω. If T_t is interpreted as a steady flow of a colorless and incompressible liquid, $f(P)$ may be regarded as an initial distribution of coloring matter in the liquid. At the time t its distribution will be given by $U_{-t}fdm$, since dm is invariant. The amount of coloring matter contained in a volume A at the time t will be (U_tf, χ_A), where $\chi_A(P) = 1$ if $P \subset \Omega$, $\chi_A(P) = 0$ if $P \subset \Omega - A$. If that content tends toward a limit, we infer from the time-average theorem

$$\lim_{t=\infty} (U_{-t}f, \chi_A) = \lim_{T=\infty} \frac{1}{T} \int_{-T}^{0} (U_tf, \chi_A)dt = (f^*, \chi_A) = \int_A f^*(P)dm.$$

Thus, if convergence takes place for any finite volume A, the density of the limiting distribution of the coloring matter is given by $f^*(P)$ being invariant under the flow, i.e., the distribution becomes stationary in the

long run. The necessary and sufficient condition for that tendency toward stationarity is that the equation

$$\lim_{|t|=\infty} (U_t f, g) = (f^*, g) \tag{2}$$

holds for any two q. s. f. $f(P)$, $g(P)$.

The equation

$$\lim_{T=\infty} \frac{1}{2T} \int_{-T}^{+T} [(U_t f, g) - (f^*, g)]dt = 0 \tag{3}$$

is a weaker interpretation of the tendency toward stationarity. However, there seem to be some indications that (3) is a more appropriate interpretation. Moreover, the integral average on the left side of (3) is the square of the dispersion of the function $(U_t f, g)$ about the value

$$(f^*, g) = (f^*, g^*)$$

so that (3) still represents "observable" convergence.

In his paper on "Complete Transitivity and the Ergodic Principle,"[6] the author has treated the case of uniform distribution in the long run. The content of this paper admits of immediate generalization and leads to the

THEOREM 1. *A necessary and sufficient condition that* (3) *be true for any two q. s. f. is that the invariance under a transformation* T_a, $a \neq 0$, *of a measurable point set, imply its invariance under the whole group* T_t.

In connection with the spectral representation of the unitary group, the obvious condition is that $\lambda = 0$ be the only characteristic value of the spectrum. If there is no tendency of any initial distribution toward a stationary one, $(U_t f, g)$ fluctuates about (f^*, g) in an asymptotically almost-periodic manner (loc. cit.[6]).

The problem may, however, be treated from another and, in the author's belief, more natural point of view. We consider the product space $\Omega \times \Omega$ of the pairs

$$\pi = (P, Q) = (Q, P)$$

of two points of Ω, *disregarding their order*. Any point set on $\Omega \times \Omega$ is then a symmetric set in the space of the ordered pairs, and any function $F(\pi)$ is a symmetric function of the ordered pair, $F(P, Q) = F(Q, P)$. The flow $T_t(P)$ on Ω implies a "product flow"

$$T_t(\pi) = (T_t(P), T_t(Q)) = (T_t(Q), T_t(P))$$

on $\Omega \times \Omega$. Furthermore, the invariant volume element dm on Ω implies an invariant volume element

$$d\mu = d\mu_\pi = dm_P dm_Q$$

on $\Omega \times \Omega$, thus yielding an invariant measure μ over $\Omega \times \Omega$ in the sense of Lebesgue. We set

$$<F, G> = \int_{\Omega\times\Omega} F(\pi)G(\pi)d\mu, \quad \Delta(F) = \sqrt{<F, F>},$$

for any two q. s. f. $F(\pi)$, $G(\pi)$ over $\Omega \times \Omega$, and

$$U_t F = F(T_t(\pi)).$$

Strong convergence of functions on $\Omega \times \Omega$ means as usually convergence in the sense of the distance Δ.

THEOREM 2. (3) *holds for any two q. s. f.* $f(P)$, $g(P)$, *if and only if any q. s. f.* $F(\pi)$ *being invariant under the product flow is the limit in the sense of strong convergence of finite sums* $\Sigma\varphi(P)\psi(Q)$, *where* φ, ψ *are q. s. over* Ω *and invariant under the given flow.*

The condition may easily be expressed in terms of invariant point sets instead in terms of invariant functions. Let $\mathfrak{N}$ be a certain totality of measurable point sets on $\Omega \times \Omega$. We say that a measurable point set B is generated by the point sets A of $\mathfrak{N}$, if B can be approximated by finite sums ΣA such that $\mu(B + \Sigma A - B\Sigma A)$ can be made arbitrarily small. Theorem 2 may then be expressed as follows:

THEOREM 3. (3) *holds for any pair of q. s. f.* $f(P)$, $g(P)$, *if and only if every point set on* $\Omega \times \Omega$ *having a finite measure* μ *and being invariant under the product flow, can be generated by the invariant product sets* $A \times A'$ *where* A *and* A' *are any two invariant sets on* Ω *with a finite measure* m.

The most interesting particular case is the case of an ergodic flow on Ω, i.e., the case where the time-average of any q. s. f. $f(P)$ is constant almost everywhere on Ω,

$$f^*(P) = \frac{\int_\Omega f dm}{m(\Omega)}.$$

According to v. Neumann[2] the necessary and sufficient condition for ergodicity is that the flow be metrically transitive, i.e., that any invariant and measurable set has either the measure zero or the measure $m(\Omega)$. From Theorem 3 we infer therefore the

THEOREM 4. *The equation*

$$\lim_{T=\infty} \frac{1}{2T} \int_{-T}^{+T} \left[(U_t f, g) - \frac{\int_\Omega f dm \int_\Omega g dm}{m(\Omega)^2} \right]^2 dt = 0$$

holds for any two q. s. f. f, g, *if and only if the product flow is metrically transitive* (*condition for the tendency toward uniform distribution*).

The proof of Theorem 3 is simplified by the use of the

THEOREM 5. *A necessary and sufficient condition that* (3) *be true for any two q. s. f. f, g, is that*

$$(f(P)f(Q))^* = f^*(P)f^*(Q)$$

holds for any $f(P)$ being q. s. over Ω.

Proof of Theorem 5.—According to

$$[(U_t f, g) - (f^*, g)]^2 = (U_t f, g)^2 + (f^*, g)^2 - 2(f^*, g)(U_t f, g)$$

and to

$$\lim_{T=\infty} \frac{1}{2T} \int_{-T}^{+T} (U_t f, g)dt = (f^*, g)$$

the equation (3) is equivalent to the equation

$$\lim_{T=\infty} \frac{1}{2T} \int_{-T}^{+T} (U_t f, g)^2 dt = (f^*, g)^2. \tag{4}$$

In setting

$$F(\pi) = f(P)f(Q), \quad G(\pi) = g(P)g(Q) \tag{5}$$

and

$$F(\pi) = f^*(P)f^*(Q), \tag{6}$$

we infer

$$\langle U_t F, G\rangle = (U_t f, g)^2; \quad \langle \tilde{F}, G\rangle = (f^*, g)^2.$$

Thus (4) may be written in the form

$$\lim_{T=\infty} \frac{1}{2T} \int_{-T}^{+T} \langle U_t F, G\rangle dt = \langle \tilde{F}, G\rangle.$$

As this equation remains true if $\tilde{F}$ is replaced by the time-average F^* of F, we conclude that the equation

$$\langle F^*, G\rangle = \langle \tilde{F}, G\rangle \tag{7}$$

together with (5) and (6) is equivalent to (3). The condition indicated in Theorem 5 is therefore sufficient.

In order to prove that the condition is necessary we use the following elementary

Lemma.—Every function $\phi(\pi)$ being q. s. over $\Omega \times \Omega$ is the limit in the sense of strong convergence of finite sums $\Sigma \pm \varphi(P)\varphi(Q)$, where the functions $\varphi(P)$ are q. s. over Ω.

This lemma is readily proved for sums $\Sigma\varphi(P)\psi(Q)$. ϕ, however, is necessarily symmetric in P, Q, thus being the strong limit of sums

$$\tfrac{1}{2}\Sigma[\varphi(P)\psi(Q) + \psi(P)\varphi(Q)]$$
$$= \tfrac{1}{2}\Sigma\{(\varphi(P) + \psi(P))(\varphi(Q) + \psi(Q)) - \varphi(P)\varphi(Q) - \psi(P)\psi(Q)\}.$$

The lemma shows immediately that (7) must be true for any q. s. f. $G(\pi)$, i.e., that $\tilde{F} = F^*$.

Proof of Theorem 3. We suppose the equation

$$(f(P)f(Q))^* = f^*(P)f^*(Q)$$

to hold for any q. s. $f(P)$. We set

$$d(\pi) = F(\pi) - \Sigma \pm f(P)f(Q).$$

If F is invariant, i.e., if $F = F^*$, we infer

$$d^*(\pi) = F(\pi) - \Sigma \pm f^*(P)f^*(Q).$$

The fundamental equation $\langle d^*, H\rangle = \langle d, H\rangle$, H being invariant, yields, for $H = d^*$,

$$\Delta(d^*)^2 = \langle d, d^*\rangle \leqq \Delta(d)\Delta(d^*),\ \Delta(d^*) \leqq \Delta(d).$$

Since, according to the lemma, $\Delta(d)$ can be made arbitrarily small, we infer the same for $\Delta(d^*)$, i.e., F is the strong limit of sums of the required kind.

Conversely, let us suppose every invariant and q. s. f. $F(\pi)$ to be the strong limit of sums of functions

$$H' = \pm h(P)h(Q),$$

$h(P)$ being invariant and q. s. over Ω. We set

$$F(\pi) = f(P)f(Q),\ \tilde{F}(\pi) = f^*(P)f^*(Q).$$

From the equations $\langle F^*, H'\rangle = \langle F, H'\rangle$ and $(f^*, h) = (f, h)$ we infer

$$\langle F^*, H'\rangle = (f, h)^2 = (f^*, h)^2 = \langle \tilde{F}, H'\rangle$$

for every H'. $\langle F^*, H'\rangle = \langle \tilde{F}, H'\rangle$ is therefore true for any invariant H, particularly for $H = F^* - \tilde{F}$, i.e., we have $\tilde{F} = \tilde{F}^*$.

v. Neumann[2] has proved that the totality of the measurable and invariant point sets on Ω possesses a basis,

$$\Omega_x,\ 0 \leqq x \leqq 1;\ \Omega_0 = 0,\ \Omega_1 = \Omega;\ \Omega_x \subset \Omega_{x'},\ x < x',$$

such that every measurable and invariant set can be generated by the sets $\Omega_{x'} - \Omega_x$. Any measurable and invariant function reduces (apart from a set of measure zero on Ω) to a function of x, where, for given P, x is determined by the inequalities

$$P \text{ in } \Omega_{x'},\ x' > x;\ P \text{ not in } \Omega_{x'},\ x' < x.$$

The proof of the following theorem offers no difficulty.

THEOREM 6. *A necessary and sufficient condition that* (3) *hold for any two q. s. f. f, g is that every measurable function* $F(\pi)$ *being invariant under the product flow reduces to a function of* $(x, y) = (y, x)$.

With regard to the particular kind of flow defined by a Hamiltonian differential system, let us apply our results to the following case. Ω is an analytic manifold and $T_t(P)$ depends analytically upon P and t. Let

$$S_x, \quad a \leqq x \leqq b,$$

be an analytic one parameter family of analytic submanifolds being invariant under the flow (the manifolds of constant energy) and exhausting Ω altogether. The equation

$$dm = dx d\sigma_x$$

determines then an invariant volume element $d\sigma_x$ on S_x. $\sigma_x(S_x)$ is supposed to be bounded, $a \leqq x \leqq b$. The invariant volume element on the invariant product set $S_x \times S_y$ is furnished by $d\sigma_x d\sigma_y$.

THEOREM 7. *A necessary and sufficient condition that* (3) *hold for any two q. s. f. f, g and that* f^* *depend but on x is that the product flow be metrically transitive on* $S_x \times S_y$ *for almost all* $(x, y) = (y, x)$ *(in the sense of the plane measure).*

This theorem indicates thus the precise condition under which any initial distribution in the phase-space tends toward a distribution whose density depends but on the energy (fundamental hypothesis of Gibbs-Lorentz).

The proof that ergodicity on $S_x \times S_y$ for almost all $(x, y) = (y, x)$ is equivalent to the fact that any measurable and invariant function $F(\pi)$ reduces to a function of x, y, offers no essential difficulties.

Let us illustrate Theorem 7 in the following well-known case (H. Poincaré, J. Kroò).[3] x, φ are polar coördinates in the plane, and Ω is the circular region $x \leqq 1$. We consider the circular flow

$$P: x, \varphi; \; T_t(P): x, \varphi + v(x)t,$$

where $v(x)$ is continuously differentiable in $0 \leqq x \leqq 1$. S_x is here the circle with the radius x, $d\sigma_x = d\varphi$ being the invariant element on S_x. The product flow on $S_x \times S_y$ is given by

$$\varphi, \psi \longrightarrow \varphi + v(x)t, \psi + v(y)t.$$

This flow is ergodic if and only if $v(x)/v(y)$ is an irrational number. The condition of Theorem 7 will therefore be fulfilled provided that $v'(x)$ has but a finite number of zeros.

The condition indicated in Theorem 7 cannot, however, be regarded as final. Tendency toward a stationary distribution depending but on x

(Gibb's canonical distribution) depends obviously upon properties in the small, i.e., upon the behavior of the flow in the shells between S_x and $S_{x+\delta}$, $a \leqq x \leqq b$, δ being arbitrarily small. The true condition for that tendency must therefore be an infinitesimal one. It is evidently of great interest to find such a condition.

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[1] Cf. B. O. Koopman, these PROCEEDINGS, **17**, 315–318 (1931).

[2] Cf. J. v. Neumann, these PROCEEDINGS, **18**, 70–82 (1932).

[3] Cf. J. W. Gibbs, *Statistical Mechanics*, Chapter VII. We refer in particular to the sections 23 and 27 of P. and T. Ehrenfest's article, "Statistische Mechanik," in the *Encyclopaedie der math. Wiss.*, IV 2.

[4] The actual existence of the limit except in a point set of zero measure has been proved by Birkhoff, these PROCEEDINGS, **17**, 650–660 (1931). This fact is, however, not needed for our purposes.

[5] An elementary proof has been given by the author, these PROCEEDINGS, **18**, 93–100 (1932).

[6] E. Hopf, these PROCEEDINGS, **18**, 204–209 (1932). The same subject has been simultaneously and independently treated by Koopman and v. Neumann, these PROCEEDINGS, March, 1932. These authors have found another interesting form of the equation (3). Furthermore, they give an example of a unitary group U_t, for which (3) holds, whereas (2) is not fulfilled in general.

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*REGULAR FAMILIES OF CURVES. II**

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The purpose of this note is three-fold: (*a*) A new definition of the function μ is given.[1] (*b*) A condition for the regularity of a family of curves is stated. (*c*) If a closed set of "invariant points" be added to a regular family of curves, an "extended family of curves" is formed; theorems are stated on the covering of the curves by a set of "tubes," and on the introduction of a function continuous throughout the extended family.

1. *The New Function* μ.—Let R be any metric separable space, and let $a_1, a_2, \ldots$, be a sequence of points dense in R. For any x in R, define $f_n(x)$ as follows:

$$f_n(x) = \frac{1}{1 + \rho(x, a_n)}. \tag{1}$$

Let S be any subset of R; we put

$$\mu_n(S) = \max_{x \subset S} f_n(x) - \min_{x \subset S} f_n(x), \tag{2}$$

and

$$\mu(S) = \sum_{n=1}^{\infty} \frac{\mu_n(S)}{2^n}. \tag{3}$$

If we restrict ourselves to closed subsets of R, and note that $|f_n(x) - f_n(y)| \leqq \rho(x, y)$, the two fundamental properties of the function μ stated in Paper I[2] are easily seen to hold. We have thus dropped the restriction that our sets be totally bounded.

We note in passing that Brouwer's Reduction theorem (see for instance, Kerekjarto, "Topologie" I, p. 45) can be proved easily with the aid of the function μ. If the set M is not irreducible, we remove from it nearly as much as possible, i.e., we take a subset with a small μ; if the resulting set M_1 is not irreducible, we take a subset of it with a small μ, etc. The limiting set M^* is easily seen to be irreducible.

2. *The Regularity of a Family of Curves.*—A necessary and sufficient condition that a family of curves be regular is that for each arc pq of a curve C and any $\epsilon > 0$ there is a $\delta > 0$ such that if $p' \subset V_\delta(p)$, then there is a point q' on the curve C' through p' such that (1) each point of one of the arcs pq, $p'q'$ is within ϵ of some point of the other, and (2) if r' and s' are on $p'q'$ and within δ of each other, then the arc $r's'$ is of diameter $< \epsilon$.

It follows that the families of curves in the examples given in Paper I are regular. We note that the curves in a regular family need not be equicontinuous, as is shown by the following example (using polar coördinates). One curve is $r = 1$; the others are $r = 1 - 1/(\theta + \gamma)$, $(\theta > 1 - \gamma)$, one curve corresponding to each γ, $0 \leqq \gamma < 2\pi$.

3. *Extended Families of Curves.*—We assume here that the regular family of curves forms an open subset R' of a compact metric space R. The remaining points $R_1 = R - R'$ we call invariant points. For instance, R might be a closed and bounded part of Euclidean n-space, and R_1, a closed subset of R. Moreover, we now restrict the curves forming R' to be images of an open segment or of a circle.

We assume also that the family of curves is orientable, that is, we can assign a direction to each curve so that neighboring curves are similarly oriented. By this we mean that the regularity condition in Paper I is satisfied, with q' lying in the positive or negative direction from p' according as q lies in the positive or negative direction from p. We shall say the curves of R' with the points of R_1 form an extended family of curves.

4. *The Tubes.*—Take a point p of a curve C, and a cross-section S_0 through p. Transforming S_0 by means of the function μ a small amount in each direction gives cross-sections S_1 and S_2. The arcs $p_1p_0p_2$, $p_i \subset S_i$, $i = 0, 1, 2$, are the arcs of the tube T containing p. We call S_1 and S_2 its ends.

In an extended family of curves there exists a sequence of tubes T_1,

T_2, ..., all lying in R', and covering R', and such that any closed set in R' has points in but a finite number of the tubes. We can give the sequence of tubes either one of the following properties: (1) Any tube contains points of at most a single end of any previous tube; (2) if the point p within the arc p_1p_2 of one of the tubes is contained in a preceding tube, then all of p_1p_2 is contained in preceding tubes.

5. *The Function f.*—In an extended family of curves a function f can be introduced with the following properties.

(1) With each point p of R and any t, $-\infty < t < +\infty$, there is associated a single point $q = f(p, t)$, which lies on the curve C through p, or coincides with p if p is an invariant point. Further, for each point q of C there is a t such that $q = f(p, t)$.

(2) $f(p, t)$ is continuous in both variables; that is, for every $\epsilon > 0$ there is a $\delta > 0$ such that

$$\rho[f(p, t), f(p', t')] < \epsilon \text{ if } \rho(p, p') < \delta \text{ and } |t - t'| < \delta.$$

(3) For any point p and any two numbers t_1 and t_2,

$$f[f(p, t_1), t_2] = f(p, t_1 + t_2);$$

also

$$f(p, 0) = p.$$

This theorem is proved by defining f successively in the tubes T_1, T_2, ..., with the second property in §4.

* Presented to the American Mathematical Society, March 25, 1932. The first paper, I, will be found in these PROCEEDINGS, 18, 275–278 (March, 1932).

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[1] The definition of μ here given was discovered during a conversation with S. Lefschetz.

[2] Equations (3) and (4).